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He who stays in the footsteps of others cannot improve

Editorial

The Sumerians wanted to do business, write down purchase and debt contracts, and to control their inventory levels. Thus they invented the cuneiform script around 3500 BC. In Mesopotamia, meanwhile, a clever friend one day had the idea to build a circular disc for force transmission and created the first wheel. Around 2900 BC, the free-turning round disc gave a fellow countryman the sudden inspiration to make a pottery wheel - and a fascinating new craftsmanship was born. In the 12th century the Arab engineer al-Dschazari thought about the first automatic timer, and he created the ‘elephant clock’. It consisted of a weight-powered water clock, designed to move and make a sound every half an hour. A reproduction of this masterpiece can be seen in the Swiss Watch Museum at Le Locle in the Jura Mountains. Or think about Gutenberg, who in the 15th century had the brainwave to use movable letters: he initiated a revolution in book printing. In 1917, Einstein said that besides absorbing and emitting light spontaneously, electrons could be stimulated to emit light of a particular wavelength. This sounds quite like the process that makes lasers possible, and it is called stimulated emission. But Princeton’s most famous guest needed a fair degree of staying power, as it took almost 40 years until his scientific colleagues could amplify those emissions to prove that the physicist was correct, finally putting lasers on the way to become the powerful and ubiquitous tools we work with today.

It is this driving force that leads to innovation: our curiosity as engineers and scientists takes us to unknown worlds, breaking down existing boundaries to create something useful; it boosts our economies, showing young people how fascinating discoveries are; and it improves quality of life, not for the chosen few who happen to live in the right place, but for anyone, anywhere around the globe.

Let’s bundle our competencies to create here, at Lake Thun, innovative novelties for promising industrial applications. In the name of the government of the Canton of Berne I wish you a wonderful stay and let’s make this conference a success!

Dr. Bernhard Pulver
Member of the Cantonal Government of Berne
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We thank our **Institutional Sponsors**

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The department of Engineering and Information Technology at the Bern University of Applied Sciences (BUAS-TI) renders services relating to education and continuing education, applied research and development, and the transfer of technological knowledge.

The core of our work centres on three aspirations:
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Competence is clearly visible in the daily contacts: Bystronic maintains a global and dense service network. Professional advice, prompt and reliable service coupled with expert maintenance are the prime characteristics of Bystronic’s customer services. Most of Bystronic’s customers are small to medium-sized companies, whether job shops or with their own products. The working day of these companies is largely characterized by a varying range of processing orders that are largely executed from “file to part”, which means they are processed from the preparation of the data, the actual manufacture and through to the final inspection stage using various technologies. With its highly-productive and user-friendly systems, Bystronic covers the complete process chain from cutting to bending and supplies the corresponding automation options as well as an integrated and open software solution.
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About Franke Artemis Group
More than 100 years ago, the Franke company under founder Walter Franke started processing metals. Histori-
cal events such as the stock market crash in 1929 along
with World War II and in later years the emergence of res-
taurant chains all had a great influence on the company’s
history of success.
Today the industrial activities of Franke Artemis Group in-
clude Franke Kitchen Systems Group and Franke Com-
cmercial Systems Group. Franke Kitchen Systems Group
is the world-leading provider of kitchen systems (sinks, taps,
water management systems, ventilation hoods, cooking
appliances). Franke Commercial Systems Group includes
Franke Foodservice Systems (systems and services for
quick service restaurants), Franke Washroom Systems
(washroom and sanitary systems in the public and semi-
public sectors), Franke Coffee Systems with a wide range of
superautomatic, professional and semi-professional
coffee machines, Franke Beverage Systems (beverage
containers) and industrial engineering.

Furthermore, Franke Artemis Group owns and manages
an extensive real estate portfolio (Franke Artemis Real Es-
tate Group) in Switzerland and abroad and holds various
strategic participations in international companies listed
on the Swiss stock exchange (Franke Artemis Asset Ma-
tagement Group). Franke Artemis Group also has a ma-
nority stake in Feintool Group, the world leader in fine blank-
ing technology.

Franke Artemis Group employs around 10,000 staff
worldwide and is established in over 40 countries with
about 80 subsidiaries. Franke Artemis Group generated
consolidated sales of CHF 2.5 billion in 2011.

Franke Industrie AG
In the early years, in particular during World War II and
afterwards, the Aarburg-based company also supplied
the Swiss Army. This cooperation had a significant influ-
ence on the early years of Franke Industrie AG (then still
Franke Industrietechnik). Back in the 1950s, combustion
chambers for the Venom and Vampire fighter jets were
being manufactured. An even more important step was the
fabrication of the afterburner section (ATAR 09C) for the
Mirage fleet of the Swiss Air Force.
In 2004, Franke Industrie AG was converted into an inde-
pendent stock corporation. Today, Franke Industrie AG fo-
cuses on the fabrication of Hot Gas Path Parts. These are
special components and assemblies used in the aeronau-
tics and space industries as well as in industrial gas turbi-
nes. The highly complex components are often exposed to
extreme temperatures of up to 1,200 ºC.

Over the course of the years, countless challenges in the
application and optimisation of processes were overcome.
A high level of technical expertise and quality is not only
expected but is set as a prerequisite by well-known cus-
tomers. A solid basis of trust is the foundation for the well-
maintained business relationships extending back many
years. Customers profit from high levels of expertise in the
processing of nickel- and cobalt-based alloys. Thanks to
the high level of technological know-how, Franke Industrie
AG works closely with its customers and subcontractors on
the development of optimal solutions, preferably in the ear-
ly development phase of projects.
Franke Industrie AG has obtained the quality certifications EN 9100:2009, ISO 14001:2008, OHSAS 18001:2007, ISO 3834-2:2005. In addition to the official certificates the company has various special approvals from well-known OEMs. Franke Industrie AG relies on its ability to supply its customers with engine-ready components. For this reason, it is essential to maintain good networks and intensive relationships with suppliers. Together with other three Swiss companies (Imbach + Cie AG, Listemann AG and Nickel Contor AG) Franke Industrie AG is active in the Turbine Components Network (TCN) www.tcn.li.

The current challenges
The basis for Franke Industrie AG’s successful business operations consists in particular of its 60 highly qualified employees. So as to be able to offer customers the best possible service in the future as well, the continuous further education of the company’s staff is of central importance. Solid knowledge of the market and maintaining partnerships going back many years are paramount for the business model. Innovative power coupled with the willingness to go the extra mile for customers are the strengths of Franke Industrie AG.

Laser applications for Hot Gas Path Parts
Hot Gas Path Parts are fabricated or cast metal components or assemblies. Their working temperature will get close to the materials specific melting point. The efficiency of an engine is in close relationship with the working temperature. Generally speaking; The higher the temperature the better the efficiency. To reduce the extreme heat in the parts cooling air holes are incorporated. The Nickel and Cobalt based alloys as well as the geometrical definition of the cooling air holes ask for special processes. In close corporation with the OEM it was decided that the best applicable way to bring in the holes is by laser drilling. The holes are drilled by Percussion and Trepanness. In special applications as Shaped Holes. The length of a laser drilled hole can be up to 23 mm (depending on material as well as hole diameter).

A superior task is to drill cooling air holes through thermal barrier coating (TBC) without delamination and excessive recast layer and microcracks. In order to verify that the accuracy of cooling air layers within the required limits the parts are being flow tested.

Laser equipment at Franke Industrie AG

3D-Laser Lasertec 130 Sauer YAG 500 W
2D-Laser truelaser 3030 CO2 / 2.7 kW

For more information about Franke Industrie AG please visit our website www.industech.ch.
LASER SYNTHESIS OF CARBON NANOSTRUCTURES

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Abstract

Versatile laser sources have been used for synthesizing carbon nanostructures, including two-dimensional graphene, one-dimensional carbon nanotubes, and zero-dimensional carbon nanoonions. Unique laser-material interactions provide versatile possibilities in synthesizing carbon nanostructures, including localized heating, direct laser writing, tip-enhanced optical near-field effect, polarization, ablation, resonant excitation, precise energy delivery, and mask-free direct patterning. Rapid single-step fabrication of graphene patterns was achieved using laser direct writing. Parallel integration of single-wall carbon nanotubes was realized using tip-enhanced optical near-field effects. High-quality carbon nanoonions were obtained through laser resonant excitation of precursor molecules.

The discovery of a series of carbon nanostructures, including C60, carbon nanotubes and graphene, opened a new era and caused several heat-waves in both scientific and engineering communities. According to their dimensionalities, carbon nanostructures can be classified into different categories, including zero-dimensional (0-D) fullerenes and carbon nanoonions (CNOs), one-dimensional (1-D) carbon nanotubes (CNTs) and carbon nanoscrolls (CNSs), and two-dimensional (2-D) graphene. The unique structures and remarkable properties of the carbon nanostructures, including electronic, thermal, mechanical and optical properties, led them to play a strong and important role in a number of scientific and engineering fields. A broad range of applications, encompassing micro/nanoelectronics, spintronics, optics, composite materials, bio-technology, environmental technology, energy storage, energy harvesting, micro/nanoelectromechanical systems, etc., have been investigated and developed based on the carbon nanostructures. It is expected that the advancements of the carbon nanostructures would provide potential solutions to meet the challenges in various fields and yield affordable products in daily life. Therefore, controlled growth and fabrication of the carbon nanostructures are required to meet the steadily growing demands.

The deployment of lasers offers unique capabilities in synthesizing carbon nanomaterials. When projected on materials surfaces, laser irradiation causes a variety of effects, including localized heating, melting, ablation, decomposition, photochemical reaction, etc., and leads to the formation of various nanostructures. Both photothermal and photochemical processes can be involved. A wide spectrum of laser wavelengths make it possible to achieve purposeful energy delivery to a target material through resonant excitation by providing photons of matching energy to interact with the target material, such as laser-induced bond breaking and bond-selective chemical reactions. Easy manipulation of laser beams stimulates the development on the mask-free direct laser writing of nanostructures. Extremely intense energy delivery through laser beams results in a rapid thermal process at the laser focal points, which provides an incomparable cold-wall rapid thermal processing technique. Polarization-dependent laser-material interactions provide unique feasibilities in the controllable fabrication of nanostructures, such as tip-induced optical near-field enhancement.

In this presentation, laser controlled growth of various carbon nanostructures will be discussed, including 1) laser-assisted direct writing two-dimensional graphene (Fig. 1), 2) controlled growth and integration of carbon nanotubes (Fig. 2), and 3) fast growth of zero-dimensional carbon nanoonions (Fig. 3).

A series of laser-assisted nanofabrication techniques have been developed for fabricating various carbon nanostructures by making use of unique laser-material interactions. Direct writing graphene patterns in a rapid single-step process was achieved through laser chemical vapor deposition, which suggests a convenient approach to achieving fast, scalable and affordable production of graphene patterns. Parallel integration of CNTs into micro/nanostructures was successfully demonstrated by making use of tip-enhanced optical near field, and suggested an efficient and cost-effective approach to fabricating and integrating CNT-based devices and circuits. In-situ removal of m-CNTs through single-step laser treatment provides a convenient approach in fabricating s-CNT-based devices. Laser-assisted growth of diameter-modulated CNTs exhibited a convenient approach to achieve bandgap engineering within single CNTs. A catalyst-free and highly efficient synthetic was developed for growing CNOs in open air through laser-assisted resonant excitation of precursor molecules. Therefore, lasers demonstrated a significant potential in the scalable and controlled growth of carbon nanostructures.
Fig. 1. Laser-assisted direct writing of two-dimensional graphene.

Fig. 2. Controlled growth and integration of carbon nanotubes.

Fig. 3. Fast growth of zero-dimensional carbon nanocones.
This presentation reviews recent advances in the basic research and development of diode pumped solid-state lasers at various wavelengths in the near infrared and visible spectral region. Tailored rare earth doped oxide and fluoride laser crystals in combination with newly available pump diode lasers in the blue and near infrared spectral region enabled the realization of highly efficient and compact solid-state coherent light sources with the laser ions Pr$^{3+}$ (green, orange, red), Yb$^{3+}$ (near infrared), Er$^{3+}$ (near to mid infrared). Recently, various efficient rare earth doped waveguide lasers have been realized by micro-structuring of bulk crystals directly with ultrafast laser pulses. Waveguide lasers with diffraction limited, fundamental modes have been obtained in channel between two parallel tracks of laser light modified material.

1. **Introduction**

Advanced laser materials, their crystal growth, spectroscopy, and the understanding of their fundamentals have opened the way for efficient laser sources at various wavelengths in the near infrared, visible, and UV spectral region, at time regimes down to femtoseconds, and power regimes up to multi-kW in continuous wave (cw) operation. High efficiencies have been achieved with diode pumped oxide and fluoride laser crystals doped with trivalent rare earth ions Nd$^{3+}$, Yb$^{3+}$, Er$^{3+}$, Ho$^{3+}$, Tm$^{3+}$, and Pr$^{3+}$. In this contribution we focus on new developments of bulk and waveguide lasers in the visible (Pr$^{3+}$) and near to mid infrared spectral range (Yb$^{3+}$, Er$^{3+}$).

2. **Yb$^{3+}$-sesquioxide lasers**

In 1991 the realization of a diode pumped Yb:YAG laser [1] at 300 K initialized a renaissance of research on Yb-doped laser materials. Yb$^{3+}$-lasers feature several important advantages: Yb$^{3+}$ ions have only two 4f-states, the ground state $^2F_{7/2}$ and the excited state $^2F_{5/2}$, separated by about 10000 cm$^{-1}$. Thus, excited-state absorption of the pump and laser radiation or up-conversion is not expected. Due to the small Stokes shift (typically 500 cm$^{-1}$) of the quasi 3-level scheme the heat generation in the lasing process is small and makes it a suitable ion for high average power lasers. Yb$^{3+}$ ions exhibit a relatively broad emission band which leads to tunability and the possibility of ultrashort pulse generation. The lifetime of the upper laser level ranges from a few hundred microseconds to milliseconds, which implies large energy storage capacity for Q-switched operation.

Crystals based on sesquioxides possess high thermal conductivities and high optical quality. The Heat Exchanger Method is used for the growth of sesquioxides like Sc$_2$O$_3$, Y$_2$O$_3$, and Lu$_2$O$_3$. Due to the high melting temperature (~2450 C) Rhenium crucibles ($T_{max} = 3180$ C) have to be used in a slightly reducing growth atmosphere. For instance Yb:Lu$_2$O$_3$ has been operated in thin-disk geometry at slope efficiencies of 85% and cw output powers of 301 W at input powers of 413 W resulting in an optical-to-optical efficiency of 73% (see Fig. 1) [2]. Furthermore, tuning of the laser output from 987 nm to 1127 nm with more than 10W of cw output power over a tuning range of 90 nm was demonstrated [3]. A mode-locked thin disk laser based on Yb:Lu$_2$O$_3$ generated pulse widths of 731 fs and 141 W of average output power at an optical-to-optical efficiency of more than 40% [4]. Recently, pulses as short as 96 fs have been achieved at an average power of 5.1 W with the gain-broadened, mixed sesquioxide LuScO$_3$ [5].
3. **Er$^{3+}$-sesquioxide lasers near 3 µm**

Lasers at wavelengths around 2-3 µm are interesting for medical applications due to the strong absorption band of water around 2-3 µm. It was shown earlier that Er-doped Lu$_2$O$_3$ exhibits interesting laser parameters for the transitions near 3-µm [6,7]. Very recently, a record cw output power of 5.9 W at a slope efficiency of 27% was achieved with laser diode pumped Er:Lu$_2$O$_3$ on the $^4I_{11/2} \rightarrow ^4I_{13/2}$ laser transition near 2.85 µm [7].

4. **Visible Pr$^{3+}$-lasers**

With respect to visible coherent light generation breakthroughs have been achieved with semiconductor pumped Pr$^{3+}$-lasers operating in the green, orange, and red spectral region. The energy level scheme of Pr$^{3+}$ offers several very efficient fluorescence and laser transitions in the blue (~485 nm), green (~525 nm), orange (~605 nm), and in the deep red (~695 nm, ~720 nm) spectral region as shown in Fig. 2 (left). Optically pumped semiconductor lasers (OPSL) operating near 480 nm as well as InGaN laser diodes emitting near 444 nm are efficient pump sources for Pr$^{3+}$. In order to avoid non-radiative $^1P_0$-$^3D_2$ decay, hosts with low phonon energies must be used. Fig. 2 (right) shows the performance of diode pumped Pr$^{3+}$:LiYF$_4$ at various wavelengths in the visible spectral region [8].

5. **Waveguide lasers**

Due to nonlinear absorption processes, volume structuring of dielectric materials on a micrometer scale is possible with ultrashort laser pulses. Focused femtosecond-pulses can create a modification of the material and can increase the refractive index by stress birefringence in the surrounding material. If two parallel tracks are written, a waveguide structure is created between the tracks. For many applications, it is advantageous to use crystalline host materials. Rare-earth-doped crystals offer higher peak cross sections and superior thermomechanical properties compared to glasses. For example, femtosecond-laser written Yb:YAG waveguide lasers have been operated at 2 W of cw output power and an optical conversion efficiency of 62% with respect to the launched pump power [9]. Recently, waveguide lasers in the visible spectral region could be realized with Pr:SrAl$_{12}$O$_{19}$ for the first time [10].

References


Coherent THz Spectroscopy and Imaging

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We review our activities in THz imaging, specifically in THz near-field imaging. We apply these techniques to various systems, such as 3D image reconstruction, chemical imaging, THz photonic crystals, or THz metamaterials. Further we demonstrate that nanostructures in thin metal sheets are promising tool for THz switching or nonlinear THz science. If designed appropriately, such structures show extremely strong field enhancements.

1. Introduction

The last decades have seen significant progress in the development of THz technologies in a variety of research fields and applications, such as chemical recognition, imaging, material inspection, or security control. THz waves cover a large region of the electromagnetic spectrum that is between the well-established microwave and infrared bands. The significance of this regime for imaging lies in the accessibility of both structural and spectroscopic information. Applications of THz imaging and spectroscopy include biomedical imaging, detection of explosives, or nondestructive evaluation tools for the aerospace industry. In THz time-domain spectroscopy, a pulsed THz field is generated and the electric field is measured. Spectral phase and amplitude information is obtained by taking the Fourier transform of the measured time domain data. There are several well-developed THz tomographic imaging methods, including THz diffraction tomography and THz computed tomography (THz-CT). We introduce here a THz imaging modality that is not limited to small dielectric constants (or refractive index) or weak scatter and uses an iterative optimization method to solve the nonlinear cost function. Imaging results presented for a two-dimensional sub-wavelength object allow exploration of the method to accurately reconstruct the dielectric constant and position, paving the way for imaging arbitrary three-dimensional objects.

Refined imaging techniques can also be used to study the interaction of electromagnetic waves with randomly or periodically structured media. Especially near-field techniques are valuable tools when the structure sizes become comparable to or even smaller than the wavelength. Examples are Photonic Crystals (PhC) which are composite materials with periodic variations of the electromagnetic properties in one, two or three dimensions. The variation of the dielectric properties forms a macroscopic periodic potential and if the variation is large enough, Bragg scattering of the interfaces causes similar phenomena, as the atomic potential does with electrons. For example, the propagation of an electromagnetic wave within such structures can be restricted. Artificially created PhCs of dielectric materials allow to observe fascinating phenomena. Field measurements become even more challenging when the structures themselves become sub-wavelength in size as it is the case in artificially created meta-materials. These materials have recently attracted considerable interest due to their potential application for perfect lensing, invisibility cloaking, or as negative refractive index materials. They typically consist of periodically arranged metallic structures such as wires or split ring resonators (SRRs), which show a strong resonant response to the electric and/or magnetic component of an incident light field. In spite of their key role direct experimental characterization methods of the microscopic near-fields remain highly challenging.

One of the major and yet unmet limitations is that, compared to the optical regime, the pulse energies supplied by current THz sources are still rather limited preventing the advent of high fidelity THz nonlinear spectroscopy. The highest average THz power levels currently available come from large-scale electron accelerators and table-top laser sources using for example large area photo-conductive switches, frequency mixing in laser-generated plasmas, or optical rectification in nonlinear crystals. To extend THz experiments into the nonlinear regime, i.e. for electric or magnetic switching applications or nonlinear spectroscopy, the quantity to be optimized is essentially the electric field strength, since a nonlinear process of order n scales with \( E_n \). The field strength is linked to the pulse energy \( Q \) through the relation \( E = \sqrt{Q/(\Delta \tau A)} \) where \( \Delta \tau \) is the pulse duration and \( A \) denotes the beam area. The available pulse energy is naturally limited by the THz system at hand and the pulses are typically already single-cycle, so that one cannot increase the field strength by adjusting the parameters \( Q \) and \( \Delta \tau \). The beam area can be minimized through tight focusing typically with parabolic mirrors. However, the diffraction limit imposes a lower boundary on \( A \), thereby restricting the obtainable field strength. Since both the electric field strength and the magnetic field scale with frequency; it is much easier to reach high fields for high frequencies. Recently, several reports have shown that the limitations due to diffraction limited focusing can be overcome by using metallic nano-structures that collect the incident radiation and focus it in a sub-wavelength volume leading to strong field enhancement. Here, we introduce different geometries in order to further increase the obtainable field enhancement. The structures are resonant in the THz regime and feature extremely small gaps. Due to the resonant behavior the resulting field strengths in the gap region are significantly higher than those for the non-resonant nano-slits. Giant enhancement factors of tens of thousands are obtained. Enhancing the field strength is one side of the medal; the other is to maximize the integrated

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nonlinear response. To that end the overall size of the volume comprising the high field strengths has to be maximized. We therefore investigate how the nonlinear response can be maximized by adjusting the structural parameters.

2. Results

We start with a THz imaging modality that gives high quality images of sub-wavelength objects at different frequencies without a requirement of low refractive index. Experiments are performed with a THz beam excitation and a scanned probe, but other illumination scanning arrangements should also be effective. Strategies for improving the highly nonlinear image reconstruction problem include the determination of an optimal prior model weight and the use of dynamic cost thresholding for improving image quality. These approaches worked well in the reconstructions we present, paving the way for faster and robust THz imaging. While a real dielectric constant is imaged, extensions to a complex dielectric constant can be achieved by imaging two real unknowns (the real and imaginary parts) at each image point. The approach can in principle be applied for the imaging of arbitrary three-dimensional objects with use of the vector wave equation. The reconstruction algorithm can also be applied to other general optimization-based inversion problems, for example, electromagnetic imaging in other frequency regimes and other modalities where a partial differential equation is used as a forward model.

In a second part we show examples of such nanostructure imaging with a focus on fundamental building blocks of meta-materials. We investigate their functioning through numerical simulations and THz near-field measurements of all three components of the electric vector field. These measurements are followed by far-field transmission measurements which are an indirect probe of the enormous THz field strength within the gap regions. In order to determine whether an induced nonlinear response will be strong enough to be detected, we exemplarily performed numerical and experimental studies where we investigate second harmonic generation (SHG) in the gap region of nano-structures filled with a nonlinear medium, here LiTaO$_3$. We show that even at moderate incident THz field strength the induced field enhancement leads to a strong SHG signal. Even though the incident electric field is only on the order of 10 kV/cm the conversion efficiency (fields) for the structures can be as high as 1%.
Construction of microfluidic biochips with enhanced functionalities using 3D femtosecond laser direct writing
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The extreme nonlinear interaction between femtosecond laser pulses and large-band-gap materials has enabled three-dimensional (3D) microfabrication inside transparent materials. In the past decade, this technique has been used for creating a variety of functional components in glass materials, including microoptics, microfluidics, microelectronics, micromechanics, etc [1]. Using these building blocks, femtosecond laser microfabrication also allows for construction of highly integrated microdevices. In this talk, we provide an overview of our latest progress made along this direction, including fabrication of integrated photonic and electro-optic devices [2-8]. In particular, we show that 3D microfluidic components with arbitrary geometries can be directly formed inside glass, allowing construction of a 3D micromixer with superior mixing performance (Fig. 1). This opens up promising prospects for a broad spectrum of applications based on compact and complex 3D microfluidic networks. Our work shows that this novel technique holds promise for fabricating 3D hybrid micro-systems, such as Lab-on-a-chip devices and Micro Total Analysis Systems in the future.

Figure 1: Schematic diagrams of the 3D passive microfluidic mixer: (a) overview and (b) close-up view images; and optical micrographs of the fabricated 3D microfluidic mixer: (c) overview and (d) close-up view micrographs. (e) 1D and (f) 3D microfluidic mixing experiments. [8]
References


Novel methods for high-speed generation of colloidal nanoparticles and large-scale periodic arrays of nanoparticles have been developed. These methods are based on laser ablation in liquids and combination of lithographic methods with laser-induced transfer [1-3]. Millions of identical nanoparticles can be transferred simultaneously by a single laser pulse. The transferred particles have spherical shape and are arranged into hexagonal arrays (Fig.1a&b). Both the nanoparticle size and period of the nanoparticle array can be independently controlled. In such nanoparticle arrays a collective plasmonic mode with diffractive coupling between the nanoparticles can be excited. Excitation of this mode leads to the appearance of a narrow (FWHM = 14 nm) resonance dip in the optical transmission spectra. The spectral position of this dip is sensitive to the refractive index changes of the local environment which is promising for sensing applications (Fig.1c). The sensitivity of $365 \text{ nm/RIU}$ and the figure of merit (FOM) of $21.5$ have been demonstrated in the visible spectral range using test water-glycerin solutions. This high sensing performance together with the fast and cheap fabrication procedure makes this nanoparticle array sensor promising for biomedical applications.

Fig.1 (a)&(b) Structure of spherical gold nanoparticles with diameters of 110 nm fabricated by a combination of nanosphere lithography and laser-induced transfer. (c) Transmission spectra of a gold nanoparticle array on a polymer substrate (similar to that in Fig 1a&b) immersed in water solutions of glycerin with different glycerin concentrations.
Time-resolved X-ray scattering using femtosecond X-ray pulses from free-electron-lasers has been applied to study the ultrafast structural response of materials after intense electronic excitation.

Ultrafast pulsed excitation of solids allows to create states of strong electronic excitation and high temperature and pressure. Subsequent to the initial deposition of energy a complex chain of secondary relaxation processes can lead to structural changes on very rapid time-scales, and often along unusual, non-equilibrium pathways. These processes have attracted continuing interest for nearly three decades, both from a fundamental physics viewpoint as well as with respect to technological applications such as laser-processing and material synthesis. The recent advent of X-ray free electron lasers (X-FELs) has offered new and fascinating possibilities in this field due to their unique combination of properties such as short wavelength, femtosecond pulse duration, extreme brightness, and spatial coherence.

In my talk I will present examples of our work performed at the XUV-FEL \textit{FLASH} (DESY, Hamburg) and the \textit{Linear Coherent Light Source} (SLAC, Menlo Park), the world's first hard X-ray FEL. Typically, thin foils of solid materials have been irradiated by femtosecond optical laser pulses. Subsequent to laser excitation the scattering of a time-delayed X-ray pulse has been observed in normal-incidence transmission geometry. Measurements of the scattering pattern as a function of the pump-probe time delay yield the transient structural changes of the material. The experiments are taking advantage of the inertial confinement of the excited samples during the first few picoseconds and provide information on the structural properties of of materials under extreme conditions of electronic excitation, temperature and pressure. Topics to be discussed include fast laser-induced melting and ablation, the formation of transient nano-scale structures (i.e. LIPPS) at laser-irradiated surfaces and the response of materials to intense X-ray excitation.
NANOSTRUCTURE FORMATION ON THE SOLID SURFACE UNDER THE ACTION OF INTENSE LASER RADIATION


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Abstract

The paper describes the mechanism for formation of periodic nanostructures on the surface of solids under the action of intense laser radiation. The model based on a nonlinear relaxation of temperature-induced stresses. The solid deformed by laser radiation is considered in a form of three simultaneously coexisting phases. The system of equations, which describes these phases, is reduced to the generalized Ginzburg–Landau equation that has a periodic solution. For estimation the calculation of the step of the periodic structure arising on the silicon surface under the action of a laser pulse is done.

1. Introduction

In recent years formation of periodic nanostructures in solids by phase transitions begin to receive more attention from researchers. For that matter developing the physical foundations of new effective methods for the formation of two- and three-dimensional structures with characteristic sizes less than 100 nm both at the surface and in the bulk of solids is of great interest. One way to solve this problem is laser treatment [1]. In the present work it is offered the mechanism for formation of periodic nanostructures on the solid surface under the action of power laser radiation, which is based on the nonlinear relaxation of temperature-induced stresses.

2. Theory

The process of deformation of a solid under sufficiently high stresses is accompanied by residual strain whose appearance is associated with both inelastic effects and the transformation of the defect structure of a crystal. The stress relaxation can be of a heterogeneous character due to the formation of novel-structure domains (relaxation domains) within the old excited structure [2]. This is associated with the collective behavior of excited atoms interacting with each other, which transforms the relaxation process into a nonlinear one. The character of dislocation domains depends on the state of the system under consideration, on conditions of the external action, and on the degree of the development of the deformation process. These domains can be centers of the new phase, groups of dislocations or disclination groups, microcracks, as well as atomic groups or vacancies forming clusters, micropores, dislocation loops, etc.

The nonequilibrium state of an elastic deformed solid is determined by its temperature \( T \), by the strain tensor \( \varepsilon_{ij} \) or by the stress tensor \( \sigma_{ij} \), and by the totality of additional internal parameters of state \( \psi_{ik}^{(1)}, \psi_{ik}^{(2)} , \ldots, \psi_{ik}^{(N)} \), that characterize the degree of the system deviation from the equilibrium state for the given \( T \) and \( \varepsilon_{ik} \). In this case, we deal with a number of parameters of state \( \psi_{ik}^{(\alpha)} \) that together with \( T \) and \( \varepsilon_{ik} \) entirely determine the state of the system. The quantities \( \psi_{ik}^{(\alpha)} \) are second-rank tensors. Let’s call them order parameters.

Hereafter we represent the entire spectrum of the relaxation parameters \( \psi_{ik}^{(\alpha)} \) via a single parameter. We choose for it the residual strain \( \varepsilon_{ij}^0(r,t) \) and the mesoscopic relaxation parameter determining the field of the relaxation process:

\[
\varphi_{ik}(r,t) = \frac{1}{V_0} \int_{V_0} \varepsilon_{ik}^0(r,t) dV ,
\]

where \( V_0 \) is the volume in which the averaging of \( \varepsilon_{ik}^0(r,t) \) is performed. Thus, the system under consideration, namely, the deformed solid, can be represented in a form consisting of three simultaneously coexisting phases. These are the relaxation field determined by the parameter \( \varphi_{ik}(r,t) \), the stress field \( \sigma_{ij}(r,t) \) corresponding to external loads, and relaxation domains of the concentration \( n \).

The time dependences \( \varphi_{ik}(r,t) , n(r,t) \) and \( \sigma_{ij}(r,t) \) are determined by the set of nonlinear differential equations
The first terms standing on the right-hand side of these equations describe, respectively, the attenuation of the relaxation process, the decay of the relaxation domains formed, and the relaxation of stresses. The description occurs in the linear approximation when mutual influence is absent. The second terms make the relaxation process nonlinear. In the first equation, this is associated with the generation of the relaxation field due to the formation of relaxation domains. The second equation allows for the effect of both the relaxation field \( \varphi_{ik}(r,t) \) and the stress field \( \sigma_y(r,t) \) on the nucleation of the relaxation domains. In the third equation, the relaxation process is stipulated by the effect of the relaxation field on the stress-relaxation rate. Here \( \gamma \), \( \kappa \), \( g_1 \), \( g_2 \), \( g_3 \) are the material constants. The quantity \( \sigma_0 \) determined by the external loads applied and corresponds to residual stresses produced as a result of the relaxation. The relaxation-field variation rate is considerably lower than that of atomic processes described by the constants \( \gamma \) and \( \nu \). This makes it possible to employ in (1) the adiabatic exclusion of variables. As a result, relaxation equation takes the form

\[
\dot{\varphi}_{ik} = A \varphi_{ik} - B \varphi_{ik}^3, \\
\dot{n} = -\gamma n + \frac{\varphi_{ik} \sigma_{ik}}{g_2}, \\
\dot{\sigma}_{ik} = \nu (\sigma_{ik} - \sigma_0) - g_3 \varphi_{ik} n.
\]

(1)

The approach described do not take into account possible spatial fluctuations of the relaxation parameter whose role grows with the elevation of external loads and temperature. Considering these fluctuations we get

\[
\dot{\varphi}_{ik} = A \varphi_{ik} - B \varphi_{ik}^3 + D \Delta \varphi_{ik}.
\]

(2)

Here \( D \) is coefficient of atom diffusion in heated crystal area. If we allow for the diffusion dispersion, Eq. (2) transforms into the generalized Ginzburg–Landau equation [3].

For \( \sigma_0 < \frac{g_2 \gamma}{g_1} \kappa \), Eq. (2) has one stable solution \( \varphi(r,t) = 0 \). In the case when the critical value is exceeded \( \sigma_0 > \frac{g_2 \gamma}{g_1} \kappa \), new “coherent” system states exhibiting spatial periodicity are realized. The period of these structures is

\[
T = \frac{\sigma_0 - \sigma_c}{2\pi \kappa} \sqrt{\frac{3}{8} \frac{D}{\nu}}.
\]

We now estimate the step of the periodic structure arising on the silicon surface under the action of a laser pulse. We assume that the residual stresses are \( \sigma_0 = 10^8 \text{N}/\text{m}^2 \), \( \kappa = \gamma = \nu = g_1 = 10^3 \text{s}^{-1} \) (since they determine the frequency of atomic transitions from one equilibrium state into another), \( g_2 \approx g_1 \approx 10^{10} \text{N}/\text{m}^2 \) are the stresses in the relaxations domains, \( D \approx 10^3 \text{cm}^2/\text{s} \) is coefficient of atom diffusion in heated crystal area. In this case the period is \( T \approx 3 \mu\text{m} \). With increasing \( \sigma_0 \), which corresponds to harder laser action, the period of structures formed must be determined by the diffusion coefficient \( D \) and by the stress-relaxation rate \( \nu \). In this case nanostructures with a period \( T \approx 50–100 \text{nm} \) arise.

3. Conclusion

In conclusion, we should note that the above consideration was performed for the three-dimensional case. We also assumed that the appearance of periodic structures in a thin near-surface layer leads to the appearance of the corresponding structures on the surface. Thus, on the basis of the approach suggested in this study, we manage to explain the appearance of nanostructures in solids under the action of an intense laser pulse. The mechanism under consideration can be realized along with other mechanisms suggested previously. The realization of this mechanism is associated with the conditions excluding the melting of the surface and its evaporation under the laser action.

References
THE CONCEPT OF CONSTRUCTION OF THE MEGAJOULE LASER INSTALLATION

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Abstract
Invited speakers (Invited Talks)
Laser systems and materials

The image of powerful laser installation with the energy of megajoule level, which will be created by the Russian Federal Nuclear Center (VNIIEF), is presented in the paper. The construction scheme of the installation is considered and the main decisions, that simplify and reduce the cost of the installation creation are presented too.
BI DOPED BULK GLASSES AND OPTICAL FIBERS. SPECIFICITIES OF SPECTROSCOPIC PROPERTIES

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The paper compares the absorption and emission properties of bulk glasses prepared by melting in a crucible and optical fibers fabricated by the powder-in-tube method. Both the bulk glasses and fibers were prepared from identical mixtures. The emission properties of the bulk samples and fibers were similar, while the "gray losses" in the fibers were an order of magnitude lower than those in the crucible melted glasses.

Keywords: bismuth-doped glass, bismuth-doped optical fiber, broadband IR luminescence

1. Introduction

The luminescence properties of bismuth-doped glasses are the subject of intense research aimed at both identifying the nature of the emission centers involved and extending the range of lasing wavelengths.¹ It is well known that the luminescence and lasing properties of Bi-doped glasses and fibers strongly depend on the conditions under which they were produced. Note in this context that the development of advanced processes for the fabrication of Bi-containing active materials with reproducible properties is a priority issue. To date, lasing and optical gain have been demonstrated in silica fibers doped with very small amounts of Bi (< 0.01 at %) and containing Al, Ge, and/or P ions or no other dopants. Most of the Bi-doped fibers reported to lase were fabricated by the MCVD process, but recent work has shown that lasing can in principle be achieved in Bi-doped fibers produced by the powder-in-tube method.² Note that no lasing of Bi-doped bulk glasses has been reported to date.

The purpose of this work was to compare the spectroscopic properties of bulk glasses prepared in a crucible to those of optical fibers fabricated by the powder-in-tube method using the same glass batch.

2. Glass composition

The bulk glasses and fiber cores had the composition 60 mol % SiO₂ + 30 mol % MgO + 10 mol % Al₂O₃ (ternary eutectic with a melting point of 1355 °C), used in the previous studies³,⁴. As shown earlier,⁵ bismuth-related active centers in glass of this composition are similar in luminescence properties to those in silica glass containing several percent alumina.⁶ The relatively low melting point of this glass composition (compared to silica glass), in combination with the high boiling points of the constituent oxides, suggests that high homogeneity can be achieved in the core of active fibers produced by the powder-in-tube method from large-particle materials. Another advantage of this composition is the high bismuth oxide solubility in it (2–3 mol % without formation of light-scattering colloidal Bi). It is worth noting here that the fabrication of optical fibers of this composition (rich in magnesium oxide) through chemical vapor deposition seems to be impossible because there are no suitable volatile Mg precursors.

3. Preparation of the bulk glasses and fibers

The starting chemicals used to prepare the glasses and fiber core materials were extra pure-grade MgO, Al₂O₃, SiO₂, and Bi₂O₃ powders ranging in particle size up to 100 μm. The powders were dry-mixed, with no liquid medium. To adequately compare the properties of the fibers and crucible-melted bulk glasses, we used the same glass batches, containing 0, 0.005, 0.025, 0.125, and 0.625 at % Bi.

The bulk glasses were prepared in a high-frequency heated iridium crucible under dry nitrogen, with an iridium stirrer used to homogenize the melt. The melt was heated to about 1800 °C.

In the fiber fabrication process, a powder mixture was placed into a tube of F300 extra pure silica glass about 9 mm in outer diameter, 3 mm in inner diameter, and 100 mm in length, sealed at one end. The tube and powder were consolidated into a fiber preform by heating in the induction furnace of a drawing tower, and the preform was then drawn into fiber. In this process, the unsealed upper end of the tube was open to the atmosphere.

4. Spectroscopic properties of the samples

Fig.1 shows the absorption spectra of the fibers and crucible-melted bulk glasses. Comparison of the spectra indicates the following:

(1) The absorption spectra of the Bi-doped fibers and bulk glasses contain bands characteristic to IR luminescence centers (500 and 700 nm) in Bi-doped aluminum containing glasses.
In the spectral range corresponding to bismuth emission (0.95 - 1.3 µm) the absorption losses in fibers were at least an order of magnitude lower than those in bulk glasses with the same doping level.

All the samples demonstrated an absorption band near 1.4 µm mostly due to the presence of OH groups. The absorption bands at 1.24 and 0.95 µm in the spectrum of the undoped fiber also arise from OH groups. The composite band around 1.1 µm in this spectrum suggests the presence of unidentified impurities.

The high optical loss in the bulk glasses seems to result from contamination with trace levels of low-valent transition metals from the crucible material. The presence of such impurities rules out lasing of the bulk glasses throughout the IR luminescence range of the bismuth centers (1.1–1.3 µm).

The high optical loss in the bulk glasses seems to result from contamination with trace levels of low-valent transition metals from the crucible material. The presence of such impurities rules out lasing of the bulk glasses throughout the IR luminescence range of the bismuth centers (1.1–1.3 µm).

5. Conclusion

Thus, the Bi-doped fibers consisting of a silica cladding and multicomponent glass core were fabricated for the first time. Their optical properties were compared with the crucible-melted bulk glasses of the same composition. The luminescence spectra of the bulk glasses and fibers were close and similar to those of MCVD-fabricated aluminosilicate fibers. The fibers produced by powder in an extra pure silica glass tube melting show not less than about one order of magnitude lower level of background losses in comparison with the bulk glasses prepared in an iridium crucible. This is some explanation for the fact that no lasing of Bi-doped bulk glasses has been demonstrated to date.

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References

Self-Q-switched Cr,Nd:ReVO₄ (Re=Gd, Y) crystal lasers

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Abstract: Self-Q-switched Cr,Nd:ReVO₄ (Re=Gd, Y) crystal lasers are demonstrated. The spectroscopic and self-Q-switched laser properties of Cr,Nd:ReVO₄ are studied. Polarized absorption spectra were measured at room temperature, which showed that the absorption bands display polarization character and an absorption band of Cr⁵⁺ ions at 1110 nm enables the crystals to be self-Q-switched laser materials. The maximum pulse energy are achieved to be 1.12 μJ with Re=Gd, and the shortest pulse width is 85.8 ns with Re=Y. The results show that Cr,Nd:ReVO₄ crystals are new potential self-Q-switched laser materials.

1. Instructions

In recent years, multifunctional laser crystals, such as the self-frequency-doubling, self-Raman conversion, self-mode locked, and self-Q-switched laser crystals, have been paid a lot of attention, because of their compactness, low loss, and simplicity in the laser design and application. In the self-Q-switching regime, neodymium (Nd³⁺) and chromium (Cr⁴⁺) co-doped YAG crystals has been investigated in detail and identified to be an excellent self-Q-switched laser material. However, due to the substitution of Cr⁴⁺ ions for a fraction of Al³⁺ ions at Al-ion sites in this crystal, Ca²⁺ or Mg²⁺ ions should also be co-doped to keep the balance of the charge, which brings some complexities in the crystal growth and problems in the applications. So it is significant to search for new self-Q-switched laser materials. Nowadays, the crystals doped with 3d⁻⁻ ions in the arrangement of tetrahedral symmetry have found potential applications as saturable absorbers for near- and mid-infrared lasers [1]. With the electronic configuration of 3d², the Cr⁵⁺ ion with a vanadate crystal as the host material should also have broad absorption in this waveband. Beside, because Cr⁴⁺ substitute for V⁵⁺ ions in those Cr⁵⁺ doped vanadates, no balancing charge is needed. Here, we report the growth, characterization and laser performance of Cr, Nd:ReVO₄ (Re=Gd, Y) crystals.

2. Experiments and results

By the Czochralski method, the Nd, Cr:ReVO₄ crystal was grown from the melts of mixed polycrystalline material NdVO₄, GdVO₄ and GdCrO₄ for Re=Gd, and NdVO₄, YVO₄ and YCrO₄ for Re=Y, under a nitrogen atmosphere containing 2% oxygen (v/v) in an iridium crucible. Figure 1 shows the as-grown Nd, Cr:ReVO₄ crystal boules with dimensions of about 30 mm × 20 mm. Observed under He-Ne laser, no light scattering is obtained, which means that the as-grown crystals have excellent quality and are suitable for the application in the laser experiment.

Figure 1. (a) As-grown crystal Nd:Cr:YVO₄ boule (b) As-grown crystal Nd:Cr:GdVO₄ boule

The polarized absorption spectra of Nd, Cr:ReVO₄ were measured with Hitachi U-3500 spectrophotometer at the wavelength of 400 nm-1500 nm at room temperature. The incident light was perpendicular to the face of the crystal during the absorption spectra measurement. The polarized absorption spectra are shown in Fig. 2. Due to the strong absorption of Nd⁵⁺ ions at about 680 nm (transmission of ³I₄/₂ to ⁵F₉/₂) for π polarization, that of Cr⁵⁺ ions at 642 nm (²A₁ to ²E) which is only allowed for σ polarization (E⊥c) is not evident. The absorption band of Cr⁵⁺ ions at 1110 nm, with the width (FWHM) of about 250 nm, is generated by the transmission of ²A₁ to ²B₂ [2] which is electric dipole allowed only for π polarization, and is not overlapped with that of Nd⁵⁺ ions at 808 nm. From the broad absorption bands near the 1100 nm for π polarization enable the crystals to be a self-Q-switched laser matrix.

The pulsed laser experimental setup is based on a two-mirror resonator with the length of about 30 mm. The pump source employed in the experiment was a fiber-coupled laser-diode with the central wavelength around 808 nm. Through the focusing optics (N. A.=0.22), the output of the source was focused into the crystal with a spot radius of 0.256 mm. For Re=Y and the output coupler (OC) of 40%, the maximum average output power of 120 mW was achieved with the incident pump power of 6.23 W. The threshold of the pulsed laser was measured to be 3.94 W. At the maximum pump power, the Q-switched pulse with the width of 173.5 ns and repetition rate of 151.4 kHz were obtained.
The energy of single pulses was 0.79 µJ. Using the pulse energy and width, the peak power was calculated to be 4.57 W. For OC = 10%, the pumping threshold is 1.53 W and the maximum output power of 103 mW was achieved at the incident pump power of 3.47 W. At the maximum pump power, the Q-switched pulse with width of 85.8 ns and the repetition rate of 293 kHz were obtained. The energy of single pulse was about 0.35 µJ much smaller than that with OC = 40% shown above. By the pulse energy and width, the peak power was calculated to be 4.09 W. The pulse width of 85.8 ns is shown in Fig. 3(a). The inset of this figure presents the pulse trains of 293 kHz. For Re=Gd, the maximum output powers of 243 and 265 mW were obtained with OC=40% and 30%, respectively, at the incident pump power of 3.2 W. The thresholds were achieved to be 1.87 and 1.43 W, and the slope efficiencies were 18.3% and 15.3%, with OC=40% and 30%, respectively. The minimum pulse widths of 230 and 362 ns were obtained with OC=40% and 30%, respectively, under the incident pump power of 2.92 W. The maximum pulse energies were gotten to be 1.12 µJ and 0.9 µJ with the two output couplers, respectively, under the respective corresponding incident pump powers of 2.6 W and 2.33 W. By the pulse energy and width, the peak power can be calculated. The highest peak power of 3.82 W was achieved with OC=40%. The pulse train with 60.2 kHz is shown in Fig.3 (b). The inset of this figure presents the pulse profile with a pulse width of 230 ns.

3. Conclusion
In conclusion, self-Q-switched Cr,Nd:ReVO₄ (Re=Gd, Y) crystal lasers are reported. The absorption band of Cr⁵⁺ ions at 1110 nm enables those crystals are self-Q-switched laser materials. With the Nd:Cr:ReVO₄ crystal, the self-Q-switched laser performance was demonstrated. All the results and discussions show that Nd, Cr:ReVO₄ are new potential passively self-Q-switched laser materials.

References
A review of the history of research and development in the field of optically pumped alkali vapor lasers and discussion of the most important achievements and existing problems in this field are presented in this talk.

Alkali vapors as a laser medium have attracted the attention of researchers since the very beginning of the laser era. It is interesting to mention that the first proposed laser was just an optically pumped alkali (potassium) laser. A.L. Schawlow and C.H. Townes proposed this laser in 1958 [1], even before the first demonstration of Ruby laser performed by T.H. Maiman in 1961 [2]. The term “Laser” was not invented yet that time and A.L. Schawlow and C.H. Townes used the term “Optical maser” to introduce a new system, which can produce “extremely monochromatic and coherent light” using “pumping with reasonable amounts of incoherent light”. Unfortunately, the alkali laser was not demonstrated at that time. The laser gain in an optically pumped alkali (Cs) vapor was first measured only in 1961 [3] and the first laser action in alkali atoms (Cs) at 7.18 μm was observed in 1962 using an RF-powered helium lamp as a pump [4]. The lasing efficiency in these experiments was very low, and the output power did not exceed 50 µW.

After these initial experiments with alkali atoms, there were various demonstrations of stimulated emission, gain and amplified spontaneous emission (ASE) in alkali vapors in the next 40 years. Numerous theoretical and experimental studies of energy transfer, energy levels mixing and a 3-level lasing in alkalis were performed during that time, but an absence of powerful enough narrowband tunable pump sources didn’t allow obtaining efficient lasing in alkali vapor until beginning of the new millennium. The comprehensive list of publications on the alkali lasers research and development can be found in reviews [5, 6].

The real interest to optically pumped alkali lasers appeared after the first demonstrations of really efficient lasing in Rb and Cs vapors that had been observed in 2003-2005 using a Ti:Sapphire laser [7, 8] and a diode laser [9] for optical pumping. This interest was stimulated by a possibility of using efficient diode lasers for pumping of alkali vapors that promised very high total wall plug efficiency for Diode Pumped Alkali Laser (DPAL). In addition, the alkali lasers promised to have a number of positive features as compared to existing high power lasers such as chemical, solid state, fiber lasers.

Alkali lasers have very high quantum efficiency: 95.3% for Cs, 98.1% for Rb and 99.6% for K as compared to 76% for a 1.06 μm Nd: YAG laser. This is very important not only for increasing the overall laser efficiency, but also for minimizing heating problems, because the energy defect is usually converted into heat released into the gain medium. Gaseous gain medium – a very important feature that allows generate laser beams with excellent spatial quality and diffraction limited divergence. In addition, it helps to reduce thermal problems existing, for example, in solid state lasers, as the gas gain medium can be flowed to remove heat. Alkali lasers can be scaled to higher powers by simple increasing the volume of a gain medium and number of pump sources. And this does not lead to the high light intensity inside the gain medium, like in fiber lasers. The latter means that nonlinear optical effects and optical damage will probably not be limiting factors for alkali lasers. Operating wavelengths of alkali lasers lie within an atmospheric transmission window. They do not use hazardous materials and can be constructed in a closed system, eliminating the need for vacuum pumping and discharge of chemicals, like in chemical lasers. All these properties and features of alkali lasers show that they can be an alternative to the most developed and successful high power laser systems and even exceed them in many parameters.

After the first demonstrations of efficient alkali lasers operation in 2003 – 2005, extensive research activity aimed on development of efficient scalable high power diode pumped alkali laser systems started. The best result obtained with a Ti:Sapphire laser pump (which is still a world record) was an 81% slope efficiency and 63% total optical efficiency for a CW operating Cs laser [10]. The first diode pumped alkali (Cs) laser [9] demonstrated a slope efficiency of 41% and an overall optical efficiency of 32%, but the output power in all these experiments didn’t exceed the 1 W level because of low pumping power. The way to significantly increase the output power of alkali lasers and the total wall plug efficiency of these lasers is through the use of high power diode laser pumping.

Diode pumped alkali lasers, or DPALs, are of particular interest because of the laser diode’s high wall plug efficiency and dependability as a pump source. Though laser diodes themselves can produce high laser powers, they lack the beam quality necessary for beam transport over large distances. DPALs can harness the optical energy of one or several laser diodes into one laser that produces a laser beam with excellent beam quality.
The main problem in using of high power diode lasers for alkali lasers pumping is to match their radiation linewidth (which is about several nm or ~1 THz) to the absorption line of the alkali atom. A typical Doppler broadened absorption line of pure alkali vapors is about 500 MHz which is many orders of magnitude less than a typical diode laser linewidth. There are several approaches for matching the diode laser emission to the alkali atomic absorption that are explored now and which allowed to demonstrate efficient Cs, Rb and K laser pumping with high power laser diodes [11 - 13].

Scaling of the alkali laser to higher powers requires the use of multiple diode laser pump sources, such as Laser Diode Arrays (LDAs) or stacks of diode laser arrays. Using of multiple LDAs for pumping alkali vapor lasers allowed to scale Rb laser to 17 W (with two LDAs pumping) [14] and Cs laser to 48 W (with 4 LDAs pumping) [15]. Transverse or side pumping of alkali gain medium allows significantly increase a number of pump sources, like it was first demonstrated in [16] for Cs laser with 15 narrowband LDA pumps.

Additional possibilities in power scaling of alkali lasers can be provided by using diode pumped alkali vapor power amplifiers, similar to demonstrated in [17], where the amplification factor of 145 for the low input signal was demonstrated. The systems with low power Master Oscillator and Power Amplifiers (MOPA) are the commonly used option in solid state laser technology. The advantage of power amplifiers is that they can preserve both the spectral and spatial beam qualities of the low power seed master laser. A chain of such amplifiers can provide significant increase of alkali lasers power.

This paper presents a review of the history of alkali laser research and development and analysis of the most important achievements in this field as well as discussion of some problems existing in this field.

References
We designed and built multi-wavelength, medical-grade optoacoustic systems. Our results obtained in pre-clinical studies in animals, healthy volunteers, patients with traumatic brain injury, anemic patients, and neonatal patients indicate that the optoacoustic systems can quickly provide real-time, continuous monitoring of important physiologic variables including venous oxygenation (both cerebral and central), and greatly facilitate prompt recognition and treatment of a variety of life-threatening illnesses in large populations of patients.
Multispectral optoacoustic tomography - volumetric color hearing in real time

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The main-stream of optical interrogations in living tissues are still limited to surface-limited microscopic imaging or otherwise low resolution diffusion tomographies. Despite significant progress in both fields, those methods do not allow exploration of the full potential of novel classes of fluorescent and other molecular agents for high-resolution volumetric quantitative imaging of entire organs, small animals or human tissues. Biomedical optoacoustics has emerged in the recent decade as a powerful tool for high-resolution visualization of optical contrast, overcoming a variety of longstanding limitations imposed by light scattering in deep tissues [1]. Optoacoustic phenomenon is unique in a way it allows to generate complete volumetric tomographic dataset from the imaged object using a single interrogating laser pulse. Furthermore, excitation at multiple wavelengths can be used in order to enable highly sensitive spectral differentiation of intrinsic biomarkers and extrinsically administered contrast agents [2]. By detecting tiny sound vibrations, resulting from selective absorption of light at multiple wavelengths, multispectral optoacoustic tomography (MSOT) can now virtually “hear color” in three dimensions [3]. The talk reviews the latest advances in optoacoustic inverse theory, spectral processing algorithms, and imaging instrumentation, which enable highly efficient volumetric imaging, real time performance and highly sensitive spectral differentiation of intrinsic contrast and exogenous contrast agents in living tissues [4]. Several in-vivo imaging studies, involving gene expression and other molecular agents, are showcased in small animals with performance that forecasts MSOT as a method of choice for biological imaging and select clinical segments as well [5].

References
CELL TRAPPING WITH PHOTOACOUSTIC READOUT:
PRELIMINARY STUDIES ON MOLECULARLY TARGETED
CIRCULATING TUMOR CELLS

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Photoacoustic (PA) imaging has been used in noninvasive molecular imaging to sense nanoparticle-targeted diseased cells providing high optical contrast in the near infrared region and sub-mm acoustic resolution up to several centimeters within the body. Unfortunately, strong background signals from tissue can easily mask the contrast agent signal. This problem is more severe when detecting rare circulating tumor cells (CTCs) in highly absorptive blood flow. In this study, the sensitivity of identifying CTCs can be improved by magnetic trapping with simultaneous PA detection by molecularly targeting CTCs with multiple functional contrast agents combining magnetic and optically absorptive gold nanoparticles. With an applied magnetic field, targeted cells accumulate and the local concentration increases, thus enhancing the PA signal. Figure 1 shows preliminary results with HeLa cells trapped in a concentration of 1 cell/ml in clear water at 6 ml/min flow, close to that in a human radial artery. By manipulating the trapped cells magnetically, the specific contrast of the targets can be enhanced by applying motion filtering on PA signals to remove highly absorptive background signals insensitive to the magnetic field, as shown in Figure 2. The new magnetomotive PA modality has great potential for clinical detection of CTCs.

Figure 1: Hela cells of 1 cell/ml trapped magnetically and identified photoacoustically. (a) Start of applying the magnetic field. (b) 68 minutes after applying the magnetic field. The triangle on the bottom indicates the permanent magnet.

Figure 2: Images of trapped Hela cells of 500 cells/ml in ink solution. Triangle indicates the magnet position. (a) Magnet in position 1. (b) Magnet in position 2. (c) Differential image of (a) and (b).
An all-optical photoacoustic (PA) imaging system based on a Fabry-Pérot ultrasound sensor was used to visualise the growth of two human tumour cell lines (K562, 293T) over time. The cells had been stably transfected to achieve the genetic expression of tyrosinase, which is involved in the production of the pigment eumelanin. The cells were injected subcutaneously into nude mice to form tumour xenografts. High resolution 3-D PA images of the tumours and the surrounding vasculature were acquired over a period of up to 26 days using visible and near-infrared excitation wavelengths. The images showed tumour growth and continued tyrosinase expression over the full duration of the study. Deep tissue imaging capabilities of the imaging system were demonstrated by detecting tyrosinase expressing cells in vivo at depths of 6–8 mm. Future applications of this technology may include investigations of cellular mechanisms, such as the development of hypoxia with tumour growth or the response to treatment.

1. Introduction

PA imaging [1] is a hybrid imaging technology, which relies on the absorption of short laser pulses to generate broadband ultrasound waves in biological tissue. The absorption-based optical contrast is encoded onto the PA waves, which are detected by ultrasound transducers at multiple points on the skin surface. From the detected PA signals, high resolution 3-D images of the absorbed optical energy distribution can then be obtained at depths well beyond one transport mean free path. This is in contrast to purely optical imaging methods, which are limited in either spatial resolution or imaging depth by the strong optical scattering exhibited by biological tissue. PA imaging has been used to visualise vascular networks in the brain [2], the skin [3], and tumours of small animals [4]. In addition, it can be used to detect and image reporter genes, which are widely used in preclinical research to study biological events such as gene expression, signalling pathways, cell proliferation and apoptosis. Genetically expressed fluorescent proteins have already been imaged in relatively transparent organisms [5]. However, relatively few fluorescent proteins provide strong absorption at near-infrared wavelengths where penetration depth in mammalian tissues is greatest [6], which restricts their potential use in mouse models to superficial imaging applications. An alternative approach to creating optical absorption in otherwise translucent cells is the genetic expression of tyrosinase, an enzyme involved in the production of the pigment eumelanin. By transiently transfecting cells, it has been shown in vitro [7] that eumelanin provides PA image contrast. However, transient transfection also results in a significant drop in the expression of tyrosinase over a period of a few days [8] therefore limiting the usefulness of this method for longitudinal studies. In this study, mammalian tumour cells were stably transduced using an integrating retrovirus to genetically express the enzyme tyrosinase. The growth of subcutaneous tumours from these cells was visualised in vivo in mice in a longitudinal study using an all-optical PA imaging system. The suitability of this technology for deep tissue imaging was also explored.

2. Methods

Figure 1 shows a schematic of the PA imaging system. Low energy excitation pulses provided by an OPO laser system were guided to the target using a multimode optical fibre. Following optical absorption in the tissue, the emitted PA waves were detected by a planar Fabry-Pérot polymer film ultrasound sensor. Its operation involves illuminating the sensor with the output of a wavelength-tuneable cw interrogation laser and detecting the intensity of the reflected light. By tuning the wavelength to the peak derivative of the interferometer transfer function, an acoustically induced modulation in the optical thickness of the interferometer produces a change in the reflected intensity which is detected by a photodiode. By raster scanning the interrogation beam across the sensor, PA signals were acquired from which 3-D images were reconstructed using time reversal techniques [9]. Integrating viral vectors were used to embed the vector transgene into the target cell genome so that cell and its progeny were permanently modified. The transgene contained the genetic information for the co-expression of not only tyrosinase but also CD34, a cell surface protein, to which a fluorescent marker was

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Figure 1 Schematic of the photoacoustic imaging system used to study subcutaneous, tyrosinase expressing tumours in nude mice. The photograph illustrates the transparency of the sensor, which allows backward mode imaging.
attached in order to sort the cells into a highly expressing population. Two cell lines (K562, 293T) were transduced. K562 are leukemia cells and 293T originated from embryonic human kidney cells. The tumours were grown subcutaneously in the flank of nude mice by injecting a suspension of 5x10^6 cells. The animals were anaesthetised using isofluorane and oxygen, and placed on the Fabry-Pérot ultrasound sensor. The tumours were imaged several times over a period of up to 26 days. Images were acquired at excitation wavelengths between 600nm and 770nm over a detection aperture of 14mm x 14mm with a step increment of 100µm. The acquisition of a single image took 8min. Histological analysis was performed on formalin fixed slices of a 293T tumour.

3. Results

Figure 2 shows x-y maximum intensity projections (MIP) of images of a 293T tumour and the surrounding vasculature acquired at different time points over a period of 26 days. The MIPs clearly show the growth of the tumour as indicated by the dashed circle, which provides a measure of the increase in the tumour diameter. Eumelanin was found to be a highly photostable compound. Extended periods of illumination with nanosecond laser pulses (around 1h per imaging session) on several separate imaging sessions did not produce evidence of photobleaching, which is often a feature of fluorescent proteins. Eumelanin provides strong PA contrast across the near-infrared wavelength region where tissue absorption is low, enabling penetration depths of several millimetres to be achieved. Histological analysis of excised 293T tumour samples showed abundant eumelanin within the tumour margins but not in other non-tumour tissue regions.

![Figure 2](image)

Figure 2 x-y maximum intensity projections of 3D photoacoustic images acquired on (a) day 7, (b) day 17, and (c) day 26 of a proliferating subcutaneous tumour formed of 293T cells (\(\lambda=640\text{nm}\)). The dashed circles around the tumour site provide an indication of the increase in tumour diameter. The cells were stably transduced to express tyrosinase, which leads to the production of eumelanin and provides the source of cellular contrast in the images.

4. Conclusions

Mammalian cells were stably transduced to express the enzyme tyrosinase, which resulted in the production of eumelanin. High resolution 3D PA images of subcutaneous tyrosinase expressing tumours were acquired in mice in vivo. The images showed tumour growth as well as the maintenance of strong tyrosinase expression during cell proliferation. Future applications of this technology may include investigations of cellular mechanisms, such as the development of hypoxia with tumour growth or the response to treatment.

References

SHOCK LASER CLEANING AND TREATMENT OF METAL SURFACES

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Laser cleaning of metal surfaces from environmental and operating contaminations becomes more and more popular nowadays. Important point that every laser action on to the surface is a combination of nonstationary and nonhomogeneous thermal and consequently mechanical action and only joint consideration can give a right results. That is why more detailed investigation of laser action on to the surface is necessary especially in the case of under the layer of the water processing.

1) The main regimes of laser cleaning such as shock waves and explosion evaporation are considered being applied to the surface contaminations.

2) Because of above mentioned reasons combined pulse laser and laser plasma action on to the surface are tested and new results are received. Among them surface refining, structuring, polishing, peening etc. with corresponding changing of mechanical, chemical and other properties. Combination of thermal and plasma-chemical action can simultaneously provide cleaning of the surface, corrosion protection, improvement of adhesion properties and increasing of surface hardness.

3) Some areas for laser cleaning of metal surfaces developed by authors are described

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INVESTIGATION AND CONTROL OF ULTRAFAST LASER-INDUCED NANOSCALE PATTERNS IN BULK DIELECTRIC MATERIALS

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1. Abstract
Local refractive index changes are the building blocks of laser-induced 3D optical functions in bulk transparent materials, e.g. fused silica. Depending on the regime of interaction, focused ultrashort pulses could induce either positive or negative isotropic smooth refractive index changes (usually denoted as type I) or produce regular nanoscale self-arranging layered structures resulting in form birefringence (type II nanogratings – Fig. 1), a regime which is regularly observed in fused silica [1,2]. Particularly the latter phenomenon is a spectacular and intriguing physical manifestation that allows the development of embedded polarization functions. A spectroscopic study is proposed to reveal the particular electronic and structural transformation of glassy matter in the self-organized subwavelength structures, indicating bond breaking and the abundance in oxygen deficiency. As the spontaneous arrangement is intermediated by electronic excitation, we equally propose a method of real time control and optimization of nanogratings formation in bulk fused silica under the action of ultrashort laser pulse with programmable variable envelopes. Relying on the advantage on the intrinsic anisotropies, the application potential in terms of polarization sensitive optical devices is discussed.

Figure 1: Typical manifestation of type II ultrafast laser-generated traces and the underlying nanogratings in fused silica. (a) Phase contrast microscopy image of trace of type II modifications. (b) Cross-section of the traces showing the nanoscale arrangement (electron microscopy). (c,d) Bulk nanograting patterns induced by radial and azimuthal polarization

References
Selective Ablation in Cu(In,Ga)Se₂ thin-film solar cells – analysis of different process regimes at sub-picosecond to nanosecond pulse duration.

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Recent achievements in Cu(In,Ga)Se₂ (CIGS) thin film technology allow the industrial production of highly efficient solar modules. A large growth of the CIGS-based solar cell production volume can be expected for the coming years thanks to some favorable properties inherent to this absorber type. A major drawback of CIGS is the inefficient patterning process. Since CIGS is a particularly difficult material for laser ablation there is still no industrial all-laser scribing solution available. Manufacturers fall back on mechanical needle scribing for the P2 and P3 scribing process and have to accept substantial broadening of the electrical interconnects due to unpredictable chipping at the scribe borders. In the present study we explored a large variety of possible processes for the P1-P3 scribing at different wavelengths and in different pulse duration regimes. Beside the direct ablation of CIGS with ultrashort pulses we also investigated more exotic processes like layer side lift-off variants. The resulting scribes were analyzed using electron microscopy (EM), laser scanning microscopy (LSM), energy dispersive X-ray spectroscopy (EDX) and electrical conductivity measurements. The most promising processes were selected for producing functional mini-modules. Multiple optimization cycles allowed us to select the processes with the best performance in the mini-module.

1. Introduction and experimental setup

Due to an unfavorable scaling law it is not possible to build large area single solar cells with high efficiency. High currents in the transparent electrical front contact would lead to considerable Ohmic losses. High efficiency on large solar modules can be achieved by dividing the module area into strips (or sub-cells) that are connected in series. Electrical interconnects between neighboring cells can be built without introducing external material just by scribing three individual lines between process steps. Along these scribes the thin films are selectively removed as illustrated in Figure 1 for a typical scribe arrangement.

![Figure 1](image-url) Cross-section through an interconnect with the three scribes P1-P3 made between the three main process steps. The P1 scribe creates an isolating line in the molybdenum-coated sheet glass substrate. Then the CIGS layer is grown on top, followed by the P2 scribe which removes the CIGS and exposes the moly back contact. In the third step, the front contact – a transparent conductive oxide (TCO) layer – is deposited and patterned in the P3 scribing process. Together, the three scribes form an electrical back-to-front contact as indicated by the dashed arrow. The non-productive area covered by the three scribes is termed the "dead zone".

While in today's production lines the P1 process is often a laser process, P2 and P3 are still mechanical needle scribes. Considerable efforts have been made to develop stable and reliable processes for P2 and P3 scribing. Various strategies were developed which employed pulsed laser sources with femtosecond to nanosecond pulse durations at different wavelengths. Promising results were reported for pulse durations of 50 ps and below [1-3], but also nanosecond pulses can lead to stable processes in some cases [4]. We conducted an extensive comparative parameter study incorporating many commercially available laser sources in order to identify and characterize stable process windows in different process and pulse length regimes. Our pre-conditions regarding the laser sources were very mild: a relatively good beam quality M²<1.5 and a near-Gaussian beam profile. The
optical system was kept as simple as possible: just a single-element focusing lens with focal length selected to produce a focal spot diameter of approximately 25 µm. Pulse durations were in the two ranges 200 fs – 50 ps and 1.5 - 100 ns. We concentrated mainly on sources emitting at 1064 nm and 512 nm but made also experiments at 1550 nm and 355 nm. All experiments were made on latest generation sample thin films grown on 50 x 50 x 1 mm³ float glass substrates at the Laboratory for Thin Films and Photovoltaics, EMPA, Dübendorf, Switzerland [5] and on industrial samples from selected manufacturers.

2. Main results

As expected the P1 process was found to be relatively uncritical in every aspect (focal position, pulse energy and wavelength) as long as the molybdenum layer was processed from the substrate side.

A much more interesting situation was found for the P2 process. We could identify two main process regimes. The first regime is observed when CIGS is directly attacked with a wavelength that is absorbed in the CIGS at pulse lengths $\geq$200 fs. By design, the CIGS acts as a volume absorber in the visible to near infrared wavelength range. This fact together with the relatively low melting point at around 1000°C makes it impossible to directly ablate CIGS without producing a fair amount of molten material. Melt can be tolerated to some extent as long as the heat affected zone does not extend into the active cell region or the neighboring scribes. Working processes in this regime are typically picosecond (10-50 ps) processes in the visible spectral range at very high overlaps $\geq$99%. The other main regime is observed when the wavelength of the laser is mismatched with the absorption spectrum of the CIGS absorber. In this case, a fraction of the pulse energy is transmitted through the CIGS and hits the molybdenum layer. The molybdenum heats up quickly at the interface and induces a large pressure gradient which can drive a lift-off process of the CIGS film. The lift-off force continuously increases with the pulse energy whereas the molybdenum layer has a relatively sharp damage threshold. The process window is limited by the minimum pulse energy necessary for the complete lift-off of the CIGS layer and the damage threshold fluence of the molybdenum layer. Well-suited laser sources for this process typically have pulse durations of a few nanoseconds. The P3 process was again found to be less critical as it is typically a lift-off process of the transparent TCO driven by a pressure gradient created at the interface to the absorbing and low-melting CIGS film.

![Figure 2](image_url)

**Figure 2** Detail of the interconnection region (electron micrograph) on a functional mini-module structured with 30 ps pulses at 1064 nm (P1) and 532 nm (P2 and P3)

Selected processes were used for producing functional mini modules. Figure 2 shows an example of an interconnect on such a mini-module. These functional mini-modules provide excellent process quality feedback as their electrical properties can be tested under standardized conditions (IEC 60904-1, AM1.5G irradiation spectrum, 1000W/m²). Based on these tests we currently run a multi-stage optimization cycle in order to find optimized process parameter that can be implemented in an industrial production machine.

References

A laser-based technique for printing transparent and weakly absorbing liquids is developed. Its principle of operation relies on the tight focusing of short laser pulses inside the liquid and close to its free surface, in such a way that the laser radiation is absorbed in a tiny volume around the beam waist, with practically no absorption in any other location along the beam path. If the absorbed energy overcomes the optical breakdown threshold, a cavitation bubble is generated, and its expansion results in the propulsion of a small fraction of liquid which can be collected on a substrate, leading to the printing of a microdroplet for each laser pulse. The technique does not require the preparation of the liquid in thin film form, and its forward mode of operation imposes no restriction concerning the optical properties of the substrate. We demonstrate that the technique is capable of printing microdroplets with good resolution, reproducibility and control, and analyze the influence of the main process parameters. The mechanisms of liquid printing are also investigated: time-resolved imaging provides a clear picture of the dynamics of liquid transfer which allows understanding the main features observed in the printed droplets.

1. Aim of the work
Laser-induced forward transfer (LIFT) is a well-developed, direct-writing technique which allows printing various materials with a high degree of precision and spatial resolution [1]. In the case of the LIFT of liquids, a laser beam is focused and absorbed at the interface between a transparent substrate and a thin film of the donor material which is going to be deposited on the receptor substrate. LIFT has been used for printing an entire range of materials: from simple aqueous-glycerol solutions, to more complex materials such as nanoparticle inks, polymers, and even biological materials, such as biomolecule solutions or living cells.

The LIFT of liquids faces, however, an intrinsic drawback related to the preparation of the liquid donor material in thin-film form, being rather difficult to obtain uniform, thickness-controlled and stable liquid films, especially when large areas or very high resolutions are involved.

In this work the development of a new laser forward printing technique is presented. The technique allows printing transparent and weakly absorbing liquids without the need for the preparation of the liquid in thin film form. The feasibility of the new technique is tested through microdroplets printing, and a study of the influence on their morphology of the main process parameters is carried out. The study is not limited to the analysis of the performance of laser printing, but a deeper understanding of the process is pursued. To this end, liquid ejection is analyzed through time-resolved imaging, a characterization technique which should help determine the mechanisms responsible for microdroplets deposition. The obtained results reveal that printing proceeds through complex dynamics which allows explaining the main features observed in the deposits.

2. Principle of operation
The principle of operation of the laser forward printing technique relies on the highly localized absorption of strongly focused ultrashort laser pulses in the close proximity of the free surface of the liquid contained in a reservoir. This results in the generation of a cavitation bubble underneath the free surface of the liquid. Once generated, the cavitation bubble expands, displacing the liquid around it. Then, a fraction of the liquid is propelled away, and collected onto a substrate. Provided that both the depth of the bubble and its pressure are the adequate ones, it can be expected that the liquid will be deposited on the substrate in the form of a well-defined droplet. For this to occur, both the laser pulse energy and focusing depth should be properly adjusted in order to allow liquid transfer devoid of splashing.

The proposed configuration which should make possible printing microdroplets of transparent or weakly absorbing liquids following the previously described principle of operation is schematized in Fig. 1. In this technique, each droplet results from a single laser pulse, and the generation of micropatterns can be achieved through the translation of the substrate respect to the laser beam.

3. Printing of droplets
The reproducibility of the technique in droplet printing is demonstrated through the preparation of large microarrays at the conditions described above, as the one depicted in Fig. 1. It can be observed that all the droplets are uniform, with a well-defined circular contour, and present small diameters (around 40 µm). Such high reproducibility demonstrates that the technique allows overcoming the drawbacks associated with the lack of uniformity and stability of the liquid film inherent to LIFT. Moreover, the in-situ control of the deposition process through a CCD camera facilitates finding the adequate printing conditions through the simultaneous adjustment of both pulse energy and focusing depth. These results demonstrate that this new printing technique indeed makes possible printing droplets with high resolution and...
reproducibility in a really user-friendly way, making unnecessary the use of printing heads or the previous preparation of the liquid in thin-film form [2]. In fact, liquids can be spotted from practically any container, like the wells of a microtiter plate, which in addition minimizes the risk of contamination.

![Figure 1: Principle of operation of the laser forward printing technique and deposited droplets](image1)

4. Liquid dynamics

Time-resolved imaging is a powerful technique to reveal the precise mechanisms responsible for material transfer during the laser forward printing of transparent and weakly absorbing liquids. As observed in the images of Fig. 2, the printing mechanism is mediated by the formation of liquid jets which result from the dynamics undergone by the cavitation bubble generated close to the liquid free surface through the subsurface focusing of the laser pulse. Such dynamics proceeds through the ejection of a first long and thin jet during bubble expansion, and through the formation of a second shorter and thicker jet which emerges from the crater resulting from bubble collapse. At low laser pulse energies the mechanism responsible for microdroplets formation is due to the contact of the first jet with the substrate, while at high energies, droplets emitted from the second jet tip during breakup also contribute to the growth [3].

![Figure 2: Time evolution of the laser generated jets; the experimental configuration corresponds to that of Fig. 1](image2)

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Laser based processes for thin film deposition

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The application of lasers for the deposition of thin films has been developed over the last decade to a variety of mature and robust techniques which are utilized for the deposition of a wide range of materials for different applications. The oldest technique for laser based thin film deposition is pulsed laser deposition (PLD). PLD is a highly flexible technique which is well suited for the deposition of thin oxide films. These films can be either applied as model systems for energy applications or can be utilized in microdevices. An alternative approach to obtain films with lateral resolution is the application of techniques where thin films with a well defined geometry are transferred from a target onto a receiver. The transfer of thin films with defined geometries has been first reported in 1969, and became known in 1986 under the name of laser-induced forward transfer (LIFT). A large number of sensitive materials, e.g. bio-materials and polymers, has been transferred by LIFT in liquid or solid form. Another approach to obtain thin structured film is post deposition structuring. One special approach has been developed for structuring of transparent materials using a liquid medium, named laser-induced backside wet etching (LIBWE).
Bi-doped optical fibers based on fused silica are broadband gain media. The optical gain spectral range is dependent on the composition of bismuth doped fiber core, which may consist of an alumosilicate, germanosilicate, phosphosilicate, or germanophosphosilicate glass. All these fibers taken together provide currently optical gain and lasing in the range from 1.15 to 1.55 μm. The efficiency of fiber lasers at a number of wavelengths has reached 50%, and output power in continuous single-mode lasing regime amounts to 20 W. Recently, in bismuth-doped germanosilicate fiber amplifier, pumped by a mere 65 mW, the 25 dB gain was attained at the central wavelength of 1440 nm in a bandwidth of 40 nm. All this points to a wide range of applications of bismuth fibers as an active media for amplifiers and lasers operating in new wavelength bands, both in the continuous mode and for the generation of ultra short pulses. In this talk the recent results on the luminescence properties of various Bi-doped optical fibers and on the development of Bi-doped fiber lasers and optical amplifiers for the spectral region 1300-1500 nm will be reviewed. The investigation of the Bi-doped fibers of simple composition is a new approach to understanding of the Bismuth active center nature.

Bismuth-doped glasses and optical fibers are new active optical materials featuring a broad luminescence spectrum in the spectral range 1000-1700 nm, the luminescence lifetime in a number of such glasses being ~ 1 ms (see, e.g., [1]). Interest in these new materials is due to the possibility to use them in lasers at new wavelengths in the near IR and for the amplification of optical signals in the range 1300-1500 nm in the next-generation of optical communication systems.
energy level schemes of Bismuth active centers (BAC) in these fibers. Higher energy levels of BACs can be obtained using $E_{\text{enh}}(\lambda_{\text{exc}}, \lambda_{\text{em}})$ under UV excitation (with the forced changing from fibers to fiber preforms). As an example, BACs in Bi-doped pure silica glass are characterized by spectra shown in Figure 1, a) and c) and energy level scheme shown in Figure 1, d). Similar results for some other promising Bi-doped fiber core compositions are now available [2, 3] and will be discussed.

After the first demonstration of Bi-doped fiber laser in 2005 [4], laser generation in bismuth-doped fibers have been obtained in the range 1150-1550 nm [1]. Recently Bi-doped fiber amplifiers with a gain of 20-25 dB under LD pump power of 460 mW and 65 mW have been demonstrated for a spectral region of 1300-1340 nm and 1409-1445 nm correspondingly [5, 6] (Figure 2, a and b). The results of all most powerful bismuth-doped fiber cw lasers demonstrated up to now are summarized in Figure 2, c.

![Figure 2: a) and b): Net gain (left scale) and noise figure (right scale) for the Bi-doped fiber amplifier: a) - Bi-Ge-P-doped fiber amplifier, pumped by 460 mW Raman laser radiation at 1230 nm. b) - GBi-Ge-doped fiber amplifier pumped by 65 mW LD radiation at 1310 nm. c) - most powerful CW Bi-doped fiber lasers demonstrated up to now. Circles with drop lines in the region (laser power>1W) indicate maximal CW output power and wavelength of the laser. Circles with drop lines at the power level of 0.2W correspond to the lasers at respective wavelengths with the output power less than 1W. Colored circled dots indicate the pump wavelength for lasers represented by the circles with drop lines of the same color.](image)

References

Powder technology and innovative fiber design enable a new generation of high-power single-mode-fiber laser sources

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By simultaneously providing ultra large mode effective area (ULMA) and close to diffraction limited laser beams, Yb-doped double-clad photonic crystal fibers have become key components for power scaling in fiber laser systems. Despite their advantages, such fibers suffer from some drawbacks among which tremendous fabrication complexity and arising costs, high bending losses and poor integrability. In this paper, we show how the REPUSIL technique, which is an alternate synthesis method to produce high-quality doped-silica, enables the design of a new generation of ULMA rare-earth-doped fibers. Some examples of innovative fiber designs will be shown and commented together with a first experimental demonstration of all-solid Yb-doped double-cladding fiber fabrication. The thermal effects, which play a major role at high power laser level and drastically compromise the single-mode regime, are also investigated. The very first experimental results for the fiber and laser characterization are given.

1. Introduction

Rare-earth-doped fiber lasers and amplifiers constantly benefit the best of fiber technology demonstrating outstanding increase of output average and peak power [1]. Fiber lasers are currently replacing bulk solid-state lasers in numerous applications [2]. This accession was particularly marked in the last ten years with the development of laser sources based on photonic-crystal-rod-type fibers exhibiting very large effective areas with core diameters up to 100µm [3]. For future power scaling of fiber lasers and amplifiers, the required effective area enlargement can be detrimental for the beam quality as the core and cladding index control become more and more critical. This is even more critical since thermal effects have been clearly identified as being responsible for strong beam quality degradations during high power operation. Temperature gradients, inducing a parabolic transversal thermal profile in the core [4] and thermally induced long-period gratings [5], are two plausible assumptions currently investigated. The extreme required precision on refractive index profile implies the use of complex manufacturing techniques that lead to exorbitant fabrication cost. Furthermore, the impact of thermal induced effects cannot be easily managed with current technology, a radical change in fabrication techniques would be a real breakthrough. In this paper, we aim to show that the REPUSIL technology makes possible the design and the development of low cost all-solid microstructured fibers for a next generation of fiber laser sources.

2. Suitable material synthesis and properties

For the fabrication of single-mode ultra-large-effective-area fibers, the accurate control of refractive index is obtained by using a risky and expensive multiple step stack and draw method. Very good index homogeneity is required as well as an accurate control of the refractive index for all material constituting the core and the cladding of such fibers. An alternate method for doped material synthesis consists in sintering and vitrifying doped powders to obtain high quality doped rods. REPUSIL method already demonstrates very good capabilities for the fabrication of efficient and homogeneous active material [6]. Figure 1.a shows an illustration of suitable doped-powders and rods. Figure 1.b shows a typical refractive index profile of vitrified doped-rods.

![Figure 1: a) Yb-doped granulate produced by a suspension doping of synthetic SiO2 particles and Yb-doped rods which are the basis for the production of laser active fibers, b) measured refractive index of powder-sinter-material (the fluctuation in the middle of the preform is a numerical artefact).](image-url)
3. Smart design and modeling
The cladding of photonic crystal fibers, made of pure silica and air holes, imply the use of index compensated doped silica in the core to satisfy suitable propagation conditions. This core material is a sub-wavelength arrangement of rare-earth-doped-silica and F-doped silica rods which require numerous delicate stack and draw operations resulting in a high cost. The use of rare-earth doped powder-sinter material as core material enables a substantial simplification of the fabrication process. As shown in figure 2, the cladding can fit all requirements if it is made of a judicious arrangement of passive index matching powder-sinter material and pure silica. Examples of fiber design and associated fabrication processes will be explained during the conference. Confinement principles and modal competition enabling single-transverse-mode emission are numerically studied and a parallel with existing standard rod-type or Large Pitch Fibers (LPF) will be done.

![Figure 2: Refractive index map and fundamental mode field intensity distribution for three examples of all-solid Large-Mode-Areas fibers: a) pure-silica-honeycomb in high refractive index material, b) large pitch fiber c) Photonic Band Gap.](image)

4. Experimental results
An all-solid LPF has been fabricated by drawing a stack of different powder-sinter rods. A 19 cell core (among which 7 central Yb-doped and 12 index matching cells) is surrounded by a structured cladding made of index matching material and 18 pure silica cells. For this first demonstration, the tube which has been used to maintain the stack is a highly F-doped tube in order to make an all-solid double-cladding fiber. Figure 3 shows the cross sections of, respectively, the structured cane and the inner cladding of the final fiber. Some parasitic air holes, that appeared during the drawing process, won't change the overall structure and don't modify its properties. They are commonly observed when plasma deposited F-doped material is drawn at high temperature.

![Figure 3: images of cross section of: a) intermediate cane and b) inner cladding of the final all solid fiber. The refractive index of the cladding is adjusted to the 7 cells Yb-doped central core](image)

5. Conclusion
Taking benefits from the opportunities offered by an alternate method to synthesis passive or active doped-silica, we propose some example of suitable ULMA rare-earth-doped-double-clad-fibers for the next generation of fiber laser sources. A first experimental fabrication standing as a proof of feasibility is demonstrated. This work, conducted under the ADVANTAGE project, is co-founded by the European Union and EOLITE Systems. EC is involved in the Region Limousin with the "Fonds européen de développement économique et régional".

References
Abstract: The purpose of this presentation is to give an overview of techniques available to produce original optical fibers and application dedicated. A brief introduction on PCF fabrication using the well-known stack and draw technique will be done, following by the interest to join this technique to other ones like Repusil® Technique, Rod in Tube and finally the Powder in Tube methods, first described by the Bell Lab in the seventies and up to date since some years by several groups in the world. Applications as light sources and optical sensors.

1. Introduction and state-of-the art

Until the end of the nineties, the most common way to obtain preforms was the MCVD process, technique leading to optical fibres with very low attenuation losses mainly developed to telecommunication applications. In 1996, Bath University re-adapted an old technique using a stack of capillaries to obtain a structured preform [1,2]. This preform is drawn and provides the famous microstructured fiber or Photonic Crystal Fiber (PCF). Besides to give a new way to produce original structures, the technique opens new field applications to scientists, no longer limited to the telecommunication domain, where attenuation losses of the fiber were not so important. Thus, in parallel of these technical developments to provide very efficient optical fibers, some groups has begun to work on the fiber material, to propose what we call ‘multi-material fibers’, where core and cladding could be in different material compositions. Some of these techniques are presented later in this paper.

1.1 Repusil® Technique

The sintering of fused silica powders is a new technique developed by the IPHT and Heraeus Quarzglas Company to produce very homogeneous rare earth doped bulk silica rods to be used as core material. The producible quantity overcomes by far the geometrical limitations of MCVD [3].

An aqueous suspension of very pure SiO$_2$ particles is doped in a similar way to the solution technique of MCVD layers [4]. The dopants were added as a mixed solution of suitable compounds of Aluminum and Ytterbium. The main difference in comparison with the MCVD technique is that the SiO$_2$ particles are homogenously dispersed in a liquid suspension and are not directly deposited within a tube. This procedure is favorable to get enough material for green body forming with typical weights of 10 to 100 g.

After some additional processing and purification steps the processed doped granulates were sintered into homogeneous and bubble free Yb-doped bulk silica rods with diameters up to 30 mm without higher radial and axial doping level variations or fluctuations of the refractive index level. For high power application up to 4 kW this technology has been proven [5,6].

This technology can be expanded to other rare earth dopants like Thulium or Lanthanum to enhance possible applications like Tm based lasers ($\lambda > 1900$ nm) or SC generation based on higher material nonlinearity

1.2 Rod in Tube method

The Rod-in-Tube method is a well-established technology for the fabrication of step index preforms and optical fibres. Due to the separate preparation of the core and cladding a wider range of material compositions and even almost non-compatible glass combinations are possible [7]. One drawback is the additional interface between core and cladding, which can cause scattering with implying additional losses. Therefore a careful preparation (grinding, polishing, cleaning) of surfaces is necessary.

A core rod has to be stacked in a geometrical adjusted cladding tube. Two ways of further fabrication are possible: i) the core / clad ensemble will be fused together on a MCVD lathe and then drawn into fibre or ii) if the expansion coefficient of core and cladding material is too different or the material is not be processed in a furnace or on the MCVD lathe, the core / cladding stack will be drawn under vacuum and melted together during fibre drawing

1.3 Powder in Tube Method

We find some information and developments of this technique in the seventies, work done by the Bell Lab when scientists tried to find the best way to obtain fibers with low attenuation losses. Unfortunately this technique couldn’t compete with a technique developed at the same time, the MCVD process. More recently, SILITEC Fibre SA, patented an original route to produce industrial preforms, using silica sand [8] to produce the cladding of the fibers. A collaboration between SILITEC and Xlim give us the possibility to adapt and develop this technique to produce core and/or cladding of the fiber with granulated glasses. Some fibers with cordierite material have demonstrated in 2008 the...
capacities of this technique to produce fibres with moderate attenuation losses (some dB/m) compatible with the targeted applications requiring only some meters of fibers (figure 1). Since some recent developments in collaboration with IPHT (Jena) give us access to heavy metal oxide glasses – Lanthanum oxide – to produce optical fibers with attenuation losses around 1dB/m [7] (figure 2). This technique can be joined with the Stack and Draw Process to obtain PCF (figure 3).

Figure 1: First optical fiber with cordierite core (10dB/m) - 2008

Figure 2: Silica doped with lanthanum oxide core (1.5dB/m) - 2011

Figure 3: A PCF fiber where silica core is replaced by a Lanthanum oxide doped silica glass - 2011

2. Application Domains

Optical source domain is very interested by the multimaterial optical fibres; we can play with the material to modify the linear and non-linear response of the guide, include rare earth-elements for amplification, or some other elements, like metallic particles, to enhance some non-linear responses. Some groups worldwide, like J. Ballato’s one from Clemson University, P. Russel’s one from Erlangen in Germany, have developed some solutions with pure Germanium or Silicium core in order to mix electronic and optical behaviour.

Another promising way for these original fibres is sensing applications. Indeed, by introducing metallic particles inside the glass matrix, we modify one physical parameter of the glass: the thermal expansion coefficient, which can provide to the fibre, an extreme sensitive answer, giving an interesting route to discriminate thermal and mechanical behaviour of fibre sensors.

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The first bismuth-doped superfluorescent fiber source operating at 1.44-µm was demonstrated. At pump power of 200 mW and pump wavelength of 1310 nm, its output signal reaches 57 mW with spectrum width of 25 nm.

1. Introduction

Superfluorescent fiber sources are widely used for many applications including optical gyroscopes and sensors, optical time-domain reflectometers (OTDRs), optical coherence tomography (OCT), and wavelength-division-multiplexing (WDM) systems [1]. Diode pumped rare-earth doped superfluorescent fiber sources (SFSs) have developed as highly stable broadband sources [2]. However, the gain bands of the rare-earth elements do not cover the full transparency range of the silica fiber, where the broadband sources are needed most. One possible candidate is the superluminescent laser diode (SLD). However, their output power is not very high and their mean wavelength exhibits a high dependence on temperature, typically 400 ppm/°C. The bismuth-doped optical fibers having a fairly wide optical gain in the range uncovered by rare earth fibers and relatively high efficiency seem promising active medium for the creation of SFS. An additional advantage is that the various glass hosts allow obtaining gain at different wavelengths: a phosphosilicate (1.3 µm), silicate (1.4 µm), aluminosilicate (1.1 µm) [3].

2. Bismuth-doped SFS

2.1 Experimental Setup

We used the double-pass backward pumped configuration to build our SFS (Fig. 1 left). The primary advantage of the double-pass configuration is its higher efficiency than one of a single-pass SFS. The length of fiber that maximizes its efficiency is shorter than for a forward SFS.

As a pump source we used Raman fiber laser at 1320 nm, but it is also possible to use commercially available semiconductor laser diode. The pump radiation was launched into the active fiber through a 1310/1480 nm WDM coupler. A Faraday rotator mirror was used at the other end of the Bi-doped fiber to reflect the ASE back. High-extinction isolator was placed at the SFS output.

Figure 1: Bi-doped SFS scheme (left). Optical loss spectrum of a bismuth-doped fiber (right)

To build an SFS with a mean wavelength of 1440 nm, we used germanosilicate Bi-doped fiber [4]. Its cutoff wavelength was near 0.9 µm. The index difference between the core and the cladding was \( \Delta n \approx 8 \times 10^{-3} \). The Bi concentration was below 0.1 wt%. The fiber optical losses were relatively low: 12 dB/km at \( \lambda = 1100 \) nm. The length of active fiber was 200 m. The spectrum of the optical loss is presented in Fig. 1 (right).

The spectra and power of the output signal were measured with optical spectrum analyzer Agilent 86140B and optical power meter EXFO FLP-650 correspondingly.

The SFS output spectra at room temperature at different pump power are shown in Fig. 2 (left). The form of output spectrum was close to the Gaussian shape. The full width at half maximum (FWHM) of 25 nm was achieved without the use of additional filters, long period gratins, pieces of passive Bi-doped fibers or other components manipulating spectrum, which are required in case of Er-doped SFS to widen output spectrum.

2.2 The Pump Power Dependences of the SFS

The spectra and the output power were measured at different values of pump power to determine the energy characteristics of the SFS. In the Fig. 2 (left) one can see that the lasing starts when the pump power is higher then 270 mW.
Fig. 2 (right) shows a plot of the SFS output power versus the pump power. The slope efficiency is about 38%. Fig. 2 (right) also shows dependence of the output spectrum FWHM on the launched pump power. The spectrum FWHM decreases when increasing the pump power and amounts to 25 nm at 260 mW. With a further increase the lasing starts. The low lasing threshold is caused by Rayleigh scattering in a long active fiber. The lasing threshold can be increased by using two-stage scheme of SFS. Fig. 3 (right) shows dependence of the output spectrum mean wavelength on the launched pump power.

### 2.3 Temperature Dependence

To measure temperature dependence of the SFS characteristics the fiber coil was placed in the thermal cycling setup. The fiber temperature was varied from -55 to 65 °C.

The spectrum forms are close to Gaussian shape and virtually remain same with the temperature. There is a slight shift of the peak and a change in the intensity. Fig. 3 (left) shows dependence of the mean wavelength and the output spectrum FWHM on the temperature. When increasing temperature, the mean wavelength of the output radiation decreases steadily from 1444 to 1440.5 nm, showing the change of 3.5 nm within the range of 120 °C. The FWHM varied from 24.4 to 26 nm.

### 3. Conclusions

In this paper we have demonstrated for the first time to our knowledge the operation of bismuth-doped SFS with mean wavelength of 1441 nm. SFS has a fairly high efficiency of 28%, maximum output power in our configuration is 57 mW at pump power of 200 mW. The temperature stability of the mean wavelength over the range from -55 to +65 °C amounts to 0.27%. The output spectrum is close to Gaussian shape with FWHM of 25 nm. The main disadvantage is the need to use the long active fiber (200 m) because of its low gain per meter. The length of the fiber is also the reason for the low lasing threshold. Further optimization of scheme configuration and optical properties of active fibers can result in the significant improvement in the Bi-doped SFS performance.

### References


HIGH POWER PHOTONIC-CRYSTAL FIBER SOURCES OF ULTRASHORT LASER PULSES

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A brief review of recent work on high power femtosecond laser oscillator, amplifier and their applications is presented. The linear and nonlinear propagation of femtosecond laser in the multi-core photonic crystal fiber are analyzed theoretically and experimentally. As a result, the performance of femtosecond lasers based on these multicore photonic crystal fibers is improved greatly.

1. Instructions
The development of high-energy and high peak power fiber laser is motivated by many scientific research and industrial applications. Recently, it has been shown by intensive research activities in the optics and optoelectronics fields that many novel properties unimaginable with conventional optical fibers can result from the photonic crystal fibers (PCFs). Based on the large mode area (LMA) single fundamental mode properties, photonic crystal fibers have been successfully applied in high power laser technology. Especially, multicore photonic crystal fibers, because of their ultra-large effective mode area and reduced heat- and stress-induced beam distortions, offer attractive solutions for power upscaling of fiber lasers and nonlinear-optical components [1,2]. Properly designed multicore PCFs can provide a larger mode area and greatly improve the performance of femtosecond fiber laser or supercontinuum generator with PCF.

2. Results and discussion
A compact nonlinear amplification without stretcher is applied in this system and phase locked amplification with multi-core large mode area PCF greatly enhances the system performance. A 150 MW peak power [2] and 50 W average power femtosecond laser are obtained respectively. High power new wavelengths, from the ultraviolet [3] to terahertz [4] and from white-[5] to black-light [6] are obtained from the PCF sources of ultrashort pulses through nonlinear process. Figure 1 shows the multicore PCFs that are applied in the high power femtosecond fiber laser amplifier system (fig.1(a)) and the power scaling of supercontinuum generation in a seven-core nonlinear PCF (fig.1(b)). The beam profiles of supercontinuum in the stable in-phase regime were recorded with a camera at the near and far field, as shown respectively in Figs. 1(c) and 1(d). Furthermore, with these new laser sources, micromachining is performed and nanoparticles are generated during the interaction between laser and materials. These results make us believe that a feasible scenario in future applications of high power femtosecond PCF laser will come soon.

Fig. 1. Scanning electron microscope image of the cross section of the seven-core LMA PCF(a) and nonlinear PCF (b). Beam profiles of the multicore nonlinear PCF supercontinuum output measured with in phase, in the near (c) and far (d) fields. The octave-spanning supercontinuum (e) generated from the seven-core nonlinear PCF.
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References


PHOTOACOUSTIC TOMOGRAPHY WITH CORRECTION FOR SPEED OF SOUND INHOMOGENEITIES

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We present an approach that accounts for the presence of speed-of-sound inhomogeneities in photoacoustic (PA) tomography. The approach is based on a measurement method that we refer to as passive element enriched photoacoustic tomography (PER-PACT) where simultaneous acquisition of SOS and PA information from subjects is possible. We excite ultrasound from a reference carbon fiber that is placed in the path of the laser source in the water in which the object is immersed. With ultrasound detection at the far-end, ultrasound transmission tomography can be performed. Simultaneously, photoacoustic data can also be acquired by the same detector, as large part of the light goes on to illuminate the object.

1. Materials and Methods

1.1 PER-PACT Experimental setup

A schematic of the PER-PACT system is shown in Fig. 1. It comprises a standard PA computed tomography (PACT) system, with object capable of rotation. The object is illuminated from 3 sides and ultrasound detection is performed using a 32 element curvilinear array in combination with a 32-channel pulse-receiver system [1] for data acquisition.

![Figure 1: Schematic of the experimental setup, with multiple side illumination](image)

The passive element is one or more strands of carbon fiber or horsetail hair [2] with a diameter of 250 μm is fixed opposite to the ultrasound transducer.

1.2 Phantoms used

As a biological specimen, we used a kidney resected from a freshly sacrificed Wistar rat. The organ was washed three times in PBS (phosphate buffered saline) solution to remove excess blood and then embedded in an agar cylinder of 26 mm diameter. The coronal plane of the kidney was imaged at 22°C with a radiant exposure of 10 mJcm⁻². Eighteen projections of the object were obtained in a slice and the signals were averaged 100 times.

1.3 Image reconstruction

**Speed-of-sound**

We used an iterative reconstruction approach in an ultrasound transmission tomography (UTT) setting [3], which uses ray refracted paths instead of straight ray paths to recover accurate SOS images of the subject. In iterative reconstructions, it is crucial to image quality that the ray integrals closely model the physical situation of energy propagation. For the forward projector we utilize the Eikonal equation which can be used to model acoustic wavefront propagation with inhomogeneous SOS distributions. The equation is solved using a high accuracy fast marching method (HAFMM).

Reconstruction of SOS compensated optical absorption distribution
In the case of stress confinement, for the inhomogeneous SOS distribution case, an approximate solution to the equation for the generation and propagation of photoacoustic waves was found by Jin and Wang as [4]:

\[ p(r, t) = \eta \frac{\partial}{\partial t} \int_{t=t_f(r', r)} A(r') \frac{dr'}{|r-r'|} \]  \hspace{1cm} (1)

where \( p(r, t) \) is the generated pressure at location \( r \) and time \( t \), \( \eta \) is a constant, \( t_f(r', r) \) is the TOF for a pressure wave to travel from point \( r' \) to point \( r \), and \( A(r') \) the optical absorption distribution. Equation (1) shows that the generated pressure can be seen as the projections over iso-TOF contours, which are determined by function \( t_f(r', r) \), which depends on the SOS distribution \( c(r) \).

From the SOS distribution ascertained above we proceed to calculate the integral over iso-TOF contours in Eq. (1). The SOS grid is resized to cover only the part occupied by the object, an area that encloses the same area as the light absorption map obtained from (simultaneous) PA measurements [5]. To obtain the TOF map for reconstruction of light absorption, we look again to solving the Eikonal equation using the HAFMM algorithm. This time from the point of view of detector positions, to calculate the integrals over the iso-TOF contours of Eq. 1. The procedure is repeated for all detector positions, resulting in \( n \) TOF maps.

2. Results

Figure 2(a) shows the SOS tomogram reconstructed from the acquired passive element data of the imaging area. All regions have the SOS expected of them. Figure 2(b) shows the PA image of the kidney reconstructed using an SOS value of 1540 ms\(^{-1}\), the commonly used value for soft tissue. The blood vessels are depicted with low contrast and blurring, with some double-line artifacts.

When we reconstruct the PA image using iso-TOFs generated from the reconstructed SOS tomogram, the image shows significant improvements (Fig. 2(c)). The blood vessels are sharp without the blurring and artifacts seen in Fig.2(b). Further, features such as interlobular, interlobar, segmental and renal blood vessels are now visible.

![Figure 2](image-url) (a) SOS map reconstructed from the acquired passive-element measurement of the imaging area, (b) PA image reconstructed with a SOS of 1540 ms\(^{-1}\), (c) SOS compensated PA image using the SOS values from (a).

3. Conclusions

We have demonstrated that the use of our PER-PACT approach, allowing simultaneous acquisition of PA and SOS information, with the use of suitable reconstruction algorithms removes degradation in PA image quality from SOS heterogeneities.

References


Laser Generated Focused Ultrasound and Detection of Ultrasound using Microring Resonators

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Optical detection of ultrasound is an emerging technique based on the interaction of strain field and optical field, modulating the optical properties of the resonance cavity for sensitive detection. Such a detection scheme can have several unique advantages, such as broadband response and size-independent sensitivity, compared with conventional piezoelectric transducers. Detector’s high sensitivity is essential for deep penetration depth, especially for high-resolution imaging because of the strong attenuation of high-frequency ultrasound. Besides, small element size has the advantage of realizing wide acceptance angle of ultrasound detection. We show highly sensitive and broad band detection of ultrasound by polymer photonic microring resonators, and demonstrate its application for high resolution photoacoustic computed tomography and photoacoustic microscopy. We also present thin-film optical transmitters to generate and focus the ultrasound, targeting high-amplitude focused ultrasound for imaging and therapeutic applications. The optoacoustic sources are made of carbon-nanotubes (CNTs) and elastomeric polymers. As the nano-composite works as excellent optical absorbers and efficient heat converters, output pressure with strong amplitudes can be generated and has a corresponding frequency spectrum showing high-frequency characteristics.

1. Instructions

Photoacoustic signals from most biological tissues have intrinsically broad bandwidth, the detection of high frequency signals remains a challenge. Conventional PZT transducers, despite their good performance at frequencies under 10 MHz, extending the operating frequency beyond 50 MHz is extremely difficult due to several reasons including the difficulty of dicing piezoceramics to micrometer size elements, electrical connections to each small elements, cross talk and electromagnetic interference, and increased noise with reduced element size. The ideal solution to address these issues is to develop an ultrasound detector with an almost flat frequency response from close to DC to very high frequency, and with sensitivity comparable or higher than conventional PZT transducers. PZT transducers can have high frequency response, however with very limited bandwidth due to the characteristics of resonant effect. It is very difficult to push the current piezoelectric transducers to GHz operation. Previous optoacoustic sensors, such as Fabry-Perot etalon, fiber gratings and dielectric multilayer interference filters, have broad receiving bandwidth but still suffer from lower sensitivity than piezoelectric transducer and therefore insufficient for detecting weak photoacoustic signals, especially for high frequency components which are attenuated quickly in tissues.

2. Polymer Microring Resonator Detector

Figure 1: Schematic (A) and SEM (b) of a microring resonator. Schematics showing resonance spectrum in transmission (c) and interaction between the waveguide and an in-coming ultrasound pulse (d). The pulse stresses the structure, deforming the waveguide and simultaneously modifying the refractive index of the core. (e) Ultrasound detection using the optical resonance of a microring sensor: (f) Frequency response of the detector (red dash) showing 90MHz bandwidth at -3dB.
We have developed a novel ultrasound detector based on polymer microring resonators,[1,2] which have shown highly sensitive detection of broad band ultrasound signals.[3] A microring resonator is composed of a closed-loop, ring-shaped waveguide (with diameter of tens to 100 micron) closely coupled with a bus waveguide which serves as input/output, as shown in Fig. 1. Resonance condition occurs when the round-trip phase acquired by the guided wave in the microring is equal to 2πm, where m is an integer. Microresonators can be used as ultrasonic detectors because their resonances can respond sensitively to the change in the effective refractive index of the guided optical mode. When acoustic pressure modulates the stress and strain in the waveguide, the change in strain results in geometric deformation which affects the effective refraction index of the guided mode. Due to its unique design and fabrication, an ultrahigh Q factor of $3.5 \times 10^5$ has recently been achieved which provides high sensitivity with a noise equivalent pressure (NEP) value of 29 Pa[4] two orders of magnitude greater than any of other existing optoacoustic detectors. With a much broader receiving bandwidth (>90 MHz at -3 dB), the microring resonators have a receiving sensitivity equivalent to or even higher than most commercially available PZT transducers of similar size. The small size of the device provides wide directivity and directly benefits photoacoustic tomography.[5] The broad band and high frequency response offers high resolution in photoacoustic microscopy, especially significantly enhancing the axial resolution of imaging.[6]

3. Optical Generation of High-Frequency and High-Amplitude Focused Ultrasound

Optoacoustic generation of ultrasound is an effective approach to obtain high-frequency acoustic waves. This approach is based on thermo-elastic volume expansion of light-absorbing medium, rather than the thickness-dependent resonance in the piezoelectric transducers. The acoustic frequency spectra can be externally controlled by the excitation light sources. A frequency range of several tens of MHz has been commonly generated by using nanosecond laser pulses. However, the weak output pressure has been a major disadvantage of optoacoustic transmitters. This is primarily due to a poor optoacoustic energy conversion efficiency ($10^{-7} \sim 10^{-8}$) determined by optical and thermal properties of the source materials. Nano-scale optical absorbers have been introduced as efficient heat converters under pulsed laser irradiation. The individual particles can work as efficient optoacoustic sources, but their utilization to realize practical ultrasonic devices requires macro-scale regulation over large areas and along specific geometries (e.g. density, orientation, and arrangement). Alternatively, the optoacoustic pressure can be boosted by increasing the excitation energy of the lasers, but the energy must be limited to avoid thermal damage on the light-absorbing sources. Due to these limitations, the optoacoustic pressure amplitudes were too weak to be used as ultrasound sources for deep tissue imaging or any therapeutic effects even when focused. Here, we demonstrate new transmitters based on CNT and polymer composite[7] using laser-generated focused ultrasound (LGFU) to achieve high-frequency and high-amplitude pressure. The LGFU demonstrates unprecedented optoacoustic pressure amplitudes by a single laser pulse. They are powerful enough to produce pronounced shock waves (>50 MPa in a positive peak per pulse) as well as acoustic cavitation.

![Figure 2. Experimental results of the laser generate focused ultrasound: (a) Time-domain waveforms around the lens focus (z = 5.5 mm) and slightly in front of the focal point (z = 5.2 mm); (b) Measured pressure amplitudes versus laser energy at focal point (z = 5.5 mm); (c) Frequency spectra for the waveforms shown in (a). Note that the sensitivity of fiber hydrophone is ~6 mV/MPa (details can be found in the experimental section). The negative amplitudes in (b) could be correctly determined only under a sub-threshold regime of acoustic cavitation.](image)

References

Abstract – Photoacoustic imaging of biological tissues using compact laser diodes instead of conventional Q-switched pulsed systems provides an attractive alternative for clinical applications. There are a number of concrete advantages including low cost, small size, high repetition rate and broad range of available wavelengths that can be utilized for the design of new biomedical imaging instrumentation. However, the relatively low power of laser diodes demands unconventional methods of photoacoustic signal generation and processing. Our approach to photoacoustic imaging utilizes irradiation using laser diodes with custom coded modulation profiles and frequency domain correlation processing of photoacoustic signals to obtain spatially-resolved images of optical contrast in tissues. This work demonstrates various methods that can be implemented in the context of correlation photoacoustic imaging to increase the signal-to-noise ratio (SNR) of correlation measurements. Particularly, we analyze various modulation waveforms (sine-wave, square-wave, pulse train and phase-coded signals) with respect to SNR optimization. Additionally, the effects of coherent signal averaging and modulation waveform parameters on photoacoustic correlation processing have been analyzed theoretically and studied experimentally.
PHOTOACOUSTIC SECTION IMAGING WITH INTEGRATING DETECTORS

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Photoacoustic section imaging is a method to visualize structures with optical contrast in selected layers of an extended object. In order to avoid resolution limitations that are due to commonly used ultrasound detectors of finite size, we propose the use of extended, integrating cylindrical elements for focusing the acoustic detection into the selected section. Imaging methods, resolution limits and results on zebra fish are demonstrated.

1. Introduction

Photoacoustic or optoacoustic imaging is a method to visualize absorbing structures in optically turbid objects [1]. It is based on the generation of acoustic waves by absorption of electromagnetic radiation. Usually, pulsed laser sources are used to irradiate the object and the emitted sound waves are measured with broadband acoustic detectors around the object to be imaged. A reconstruction algorithm is used to localize the absorbing structures. The method is very promising for the imaging of biological tissue. For three-dimensional (3D) tomography, the amount of data needed for a reconstruction is very large. An alternative is two-dimensional (2D) section imaging, where the detection of acoustic waves is limited to a section or thin slab of the investigated object [2][3]. This is achieved by use of cylindrical lens detectors, which are rotated or arranged on a circle surrounding the object. Reconstruction of the deposited electromagnetic energy within the section is done by back projecting the recorded signals onto circles around the detector positions with radius \( c \cdot t \), where \( c \) is the speed of sound and \( t \) the time after the laser pulse, the time of flight of the acoustic wave from a source to the detector. Such a back projection is, however, only exact if the sensor has negligible size and can be assumed to be a point. If this is not the case, the image becomes blurred at the periphery, at points lying at some distance from the center of the detection circle [4].

A way to avoid this blurring is the use of extended detectors. These integrating detectors are larger than the object [5]. Two detection setups are presented: A cylindrical, lens less detector employing a piezoelectric polymer film and an elliptical cylinder acting as acoustic reflector, combined with an optical interferometer as acoustic sensor.

2. Experimental setup

The two kinds of tomographic imaging devices are shown in Fig. 1. The lens less cylindrical detector in Fig.1(a) is a piezoelectric polymer film (PVDF) on a concave cylindrical surface. The length of the cylinder exceeds the size of the object, which is rotated about an axis perpendicular to the cylinder axis during data acquisition. Because of the integration along the length of the cylindrical surface, the signal at a given time and at a given rotational angle is closely related to the integral of the acoustic source along a line. Image reconstruction consequently uses the inverse Radon transform.

Figure 1 (a) Piezoelectric, lens less cylindrical detector. The curved area is covered by a piezoelectric polymer film. (b) Detector using an acoustic mirror (AM) having the shape of an elliptical cylinder. An optical beam along focal line F1 is the sensing element. LSI: line shaped illumination, RA: rotation axis.

The second setup shown in Fig.1(b) consists of an elliptical cylinder acting as an acoustic reflector. In one focal line of the ellipse the detector is located, which is an optical beam within a Mach-Zehnder interferometer. The object is located...
near the second focal line of the ellipse. Due to the finite aperture of the reflector, the focusing volume is extended around F2. The time of flight is proportional to the distance from the detector. Again, the device integrates along one direction and the reconstruction uses the inverse Radon transform.

For acquiring an image, the samples were illuminated by pulses from a pulsed laser source with 10 ns pulse duration at a wavelength of 500 nm. Using cylindrical lenses, the illumination was concentrated on a sheet within the imaged section. With the laser running at a repetition rate of 10 Hz, signals were acquired while the sample was rotated by \(360^\circ\) with an increment of 0.9°.

3. Results and discussion

Figure 2 shows images of a zebra fish, taken with the piezoelectric detector (a) and the optical detector (b). In both cases, a series of sections was imaged, showing various inner structures of the fish and also the black stripes on the skin. The images look quite similar, with approximately similar resolution, which was also measured in separate experiments. However, it has turned out that from the two demonstrated setups the one using optical detection has the slightly better sensitivity. Special attention is paid on the signal processing preceding the inverse Radon transform. For the lens less PVDF detector the optimum results are achieved with the Abel transform, which converts the pressure signals into signals corresponding to the mean value of the initial pressure in direction of the cylinder axis. In the case of the elliptical reflector, the best results were achieved by applying the Hilbert transform on the data before the inverse Radon transform.

Further work will be devoted to special reconstruction algorithms, which should improve the out of plane resolution (currently in the range of 1 mm).

Fig. 2 Photoacoustic section images of a zebra fish, measured (a) with the piezoelectric detector, (b) with the optical detector and the acoustic reflector.

References


Progress in real-time photoacoustic imaging using optical ultrasound detection

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Optical phase contrast full field detection in combination with a CCD-camera can be used to record acoustic fields. This allows to obtain two-dimensional photoacoustic projection images in real-time. The present work shows an extension of the technique towards full three-dimensional photoacoustic tomography. The reconstruction of the initial three dimensional pressure distribution is a two step process. First of all, projection images of the initial pressure distribution are acquired. This is done by back propagating the observed wave pattern in frequency space. In the second step the inverse Radon transform is applied to the obtained projection dataset to reconstruct the initial three dimensional pressure distribution. An experiment is performed using a phantom sample which mimics the properties of biological samples to show the overall applicability of this technique for real-time photoacoustic imaging.

1. Introduction

Charge coupled device (CCD) cameras as acoustic sensors in photoacoustic imaging (PAI) have parallel detection capabilities but at very limited camera frame rate. Therefore, an alternative approach to speed up the data acquisition is to use the spatial information content of a single captured image at a certain time instead of using time resolved signals recorded at defined detector positions. Under certain conditions a single captured image of the acoustic wave pattern contains all information to reconstruct a two-dimensional (2D) photoacoustic projection image of the initial pressure distribution. The proof of principle for use of a CCD camera in real-time PAI has already been demonstrated [1-2].

The method proposed here uses an interferometric setup for detecting pressure induced variations of density and refractive index in a coupling medium around the imaged object. If the pressure induced optical phase shift of the probe laser beam is much smaller than π, interferometry delivers a linear relation between the detected light intensity and the pressure values. This relationship is based on a linear dependence of the change of optical refractive index on acoustic pressure. The phase contrast technique, developed by Fritz Zernike, uses the interference between diffracted and non-diffracted light in an optical imaging setup and also delivers a contrast in the captured images which is proportional to the pressure amplitude [3-4].

The gained information about the optical phase shift is therefore a representation of the pressure field at a given time, projected or integrated along a certain direction. This method is related to the concept of using integrating line detectors in PAI [6-8]. Instead of a single detector that measures time resolved signals from a single line detector (a free or guided light beam), full field detection (FFD) uses a detector array, interrogating the integrated pressure at a given time from a 2D array of line detectors. To obtain the initial three dimensional (3D) pressure distribution, first of all the acoustic wave pattern has to be captured from several directions. Each individual pattern is used to calculate a 2D projection of the pressure distribution at time zero. The second step is to apply the inverse Radon transform (RT) to the projection dataset calculated in the previous step, to obtain the initial 3D pressure distribution.

2. Measurement setup

The experimental setup for capturing a picture of the acoustic wave pattern (the phase object) is shown in Fig. 1. Laser pulses with 10ns pulse duration coming from the frequency doubled output (532 nm) of a 10Hz Nd:YAG laser system were used for photoacoustic excitation. The sample was illuminated from bottom-up with a fluence of 20 mJ/cm². The sample itself was only slightly dipped in water for acoustic coupling and positioned in the rear focal plane (object plane) of the Fourier transforming lens (L2). The pulsed probe laser beam coming from a diode pumped solid state laser system (λ_rad=527 nm, τ_puls=8 ns) was collimated and expanded to a beam diameter which was about two times the size of the sample. This ensured that the detection aperture is sufficiently large to capture the outgoing acoustic waves coming from the optically absorbing regions inside the sample.

Due to interaction of the acoustic and optical fields (elasto-optic interaction) the latter attains a phase variation proportional to the pressure integrated along the probe beam path. This is converted into a measurable intensity modulation by arranging an optical signal processing element (PP: phase plate) in the Fourier plane of the first imaging lens (L2). Like in optical phase contrast microscopy an additional relative phase shift of either plus or minus π/2 between the non-diffracted and diffracted portions of the probe laser beam leads to constructive or destructive interference between both parts. This results in a so called positive or negative phase contrast image. The lens L3 is arranged in a way that its rear focal plane and the phase plate coincide, producing a reversed image of the phase object on the CCD element of the camera. Snapshots of the pressure distribution were taken with a CCD camera (pco.2000s, 14 Bit dynamic range) at certain time delay with respect to the excitation laser pulse. The time delay was adjusted by using a delay generator.
3. Experiments

To verify that the proposed method is suitable for real-time PAI an experiment was conducted using a phantom sample containing black horse hair bristles with diameters ranging from 250-300 µm embedded at a depth of 5 mm in turbid gelatin forming the letters “PA” (see inset in Fig. 2). Before reconstruction, wave pattern images were corrected by subtracting the corresponding background image. Each projection image was obtained in real-time (without averaging). To obtain the 3D image 200 projection images were recorded over a full rotation. Consequently, the recording time of the 3D data takes just 40 seconds (for wave pattern images and background images). Maximum amplitude projection images of the 3D image are shown in Fig. 2.

![Fig. 2 Maximum amplitude projection images in x, y, and z direction. The inset shows a photograph of the phantom sample. For the photograph the top layer of turbid gelatin was removed.](image)

4. Conclusion

In conclusion, the presented technique provides real-time 2D and fast 3D photoacoustic imaging using a purely optical, parallel detection method. It combines the advantages of optical detection with the possibility to acquire the required high amount of data within a relatively short time using parallel detection with a CCD camera.

References

DEVELOPMENT OF SURFACE ACOUSTIC WAVE SENSOR PLATFORMS UTILIZING LASER BASED METHODS

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Abstract
The possibility to apply laser-induced forward transfer (LIFT) for printing chemoselective polymer pixels on surface acoustic wave sensors (SAW) for toxic agents detection is presented in this study. The performance, i.e. the sensitivity, resolution, and response time, of the laser-printed devices was evaluated after a detailed optimization of the polymer coating process, with respect to the thickness, homogeneity and the area of the film coating. Tests with different toxic agents (DMMP, DCM, and EtOAc) on the sensors with the laser printed polymers revealed a very good performance of the SAW resonator arrays, in particular it could be shown that the sensors have a very high sensitivity to DMMP gas, i.e. for concentrations in the range of a few ppm.

1. Introduction
Increased selectivity, response speed, and sensitivity in the chemical and biological determinations of gases and liquids are arguably an important step toward the future micro sized sensing structures. Herein we describe new opportunities in the research of “soft” sensorial materials that have been opened up through the use of lasers.

2. Experimental
We envision that by means of matrix assisted pulsed laser evaporation (MAPLE) and laser induced forward transfer (LIFT), polymer “pixels” are precisely deposited/printed on micro sized chemoselective sensor arrays. MAPLE is a physical vapor deposition method, similar to the conventional pulsed laser deposition (PLD) that involves diluting the material of interest in a volatile, noninteracting matrix or solvent (0.1 –5 wt%) freezing the mixture to create a solid target. When the system is irradiated by a laser beam, the solvent evaporates whereas the molecules of interest (polymer or biological compounds) are collected on a substrate. [1]

In LIFT the material is transferred by the laser beam from a transparent support or donor onto an appropriate substrate or receiver. The donor substrate can be previously coated with a polymeric layer, which is called dynamic release layer (DRL) or sacrificial layer. This layer has the purpose to improve the process efficiency and to reduce the risk of damaging the layer to be transferred. [2, 3]

An important opportunity arises from the applicability of polymers to SAW sensors, i.e. 2-port resonator SAW devices operating at approximately 392 MHz were fabricated and then coated with chemoselective polymers, i.e. polyepichlorhydrine (PECH), polyisobutylene (PIB), and polyethylenimine (PEI). The three polymers were deposited by LIFT as well defined rectangular pixels on very sensitive interdigital transducers (IDTs) of the SAW resonators. To this end, challenges and future directions are discussed from the point of view of both applicability and strategies for polymer patterns.

3. Results
First, a parametric study (i.e. laser wavelength, laser fluence, target film morphology and thickness) has been carried out to determine the optimum experimental conditions under which sensitive polymer pixels may be obtained. Following the morphological and structural characterization, the performance, i.e. the sensitivity, resolution, and response time, of the laser-printed devices was evaluated after a detailed optimization of the polymer coating process, with respect to the thickness, homogeneity and the area of the film coating.

The sensor platform has been tested upon exposure to dimethyl methylphosphonate (DMMP, a simulant for nerve gases and pesticides containing phosphonate ester groups), dichloromethane (DCM, an industrial applied toxic compound and simulant for choking agents, such as chlorine or phosgene), and ethyl acetate (EtOAc, a wide spread solvent in medical and industrial applications which can be harmful to humans) vapors, showing, for each of the sensors, a different sensitivity to the selected chemical agents. (See Figure 1, 2, and 3) The best sensitivities for DMMP and DCM, obtained by using a PECH coated sensor, are 66.23 Hz/ppm and 0.034 Hz/ppm respectively, whereas the best sensitivity for EtOAc, obtained using PIB, is 0.33 Hz/ppm.

4. Conclusions
Tests with different toxic compounds on the sensors with the laser printed polymers revealed a very good performance of the SAW resonator platform, in particular it could be shown that the sensors have a very high sensitivity to DMMP and DCM gas, i.e. for concentrations in the range of a few ppm.
Figure 1 Response curves for PECH, PEI, and PIB sensors upon exposure to different concentrations of DMMP.

Reference:
INFLUENCE OF THE PRE-TREATMENT OF GLASS SUBSTRATES ON LASER-INDUCED BACKSIDE WET ETCHING USING NIR NANOSECOND-PULSES AND CU-BASED SOLUTIONS

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Laser induced backside wet etching has shown to be a promising tool for the micro-structuring of transparent materials. Several detailed studies have been performed using UV excimer laser sources, aromatic hydrocarbon and liquid heavy metal absorbers. For industrial applications it would be preferable to be able to use nano-second pulses in the near-infrared regime and “easy to handle” absorber liquids. We therefore investigated the ablation process on soda lime glass substrates for 1064 nm nanosecond-laser pulses and aqueous CuSO₄-based solutions. To study the influence of the pre-treatment of the transparent substrate on ablation, experiments were done on untreated and silanized soda lime glass surfaces. Our results show that depending on the absorber liquid the silanization of the substrate either enhances or delays the ablation. Possible ablation models for the different experimental settings will be discussed.

1. Introduction

One application for modern laser surface processing is the micro-/nanostructuring of transparent materials. Especially micro-optics and -fluidics call for high precision, crack free, smooth machining techniques. Most commonly, this is done by photolithographic etching which is very well suited for mass production. For prototyping however, techniques using laser beams are promising alternatives. A special approach suited for transparent materials is laser induced backside wet etching (LIBWE). In a typical LIBWE experiment laser light is directed through a transparent material and is absorbed in a liquid at the back side of the transparent material [1]. Depending on the used laser light and the absorbing liquid, thermal effects or shock waves lead to micro-ablation at the rear side of the glass surface. Using LIBWE, a variety of micro-optical structures with good optical properties have been manufactured by other groups using UV excimer lasers and mask projection (see e.g. [2]). Few groups made an approach with Q-switched frequency-doubled or -quadrupled Nd:YAG or Nd:YVO₄ lasers and galvoscanner-based point scanning systems [3, 4].

In recent work our group investigated LIBWE using nanosecond laser pulses at 1064nm wavelength and aqueous CuSO₄-based solutions as absorber liquids [5, 6]. We could demonstrate that smooth and controlled ablation can be achieved by using aqueous CuSO₄. Our experiments indicate that Cu²⁺ ions from the solution adsorbed on the soda lime glass surface are responsible for the ablation process [5]. The aim of this paper is to discuss the effect of a surface pre-treatment on the ablation mechanism. For this purpose LIBWE experiments were done on untreated and silanized soda lime glass substrates. As absorber liquids we choose aqueous CuSO₄ and aqueous Cu²⁺ tartrate-complex (labeled in the following as CuL₂) and with formaldehyde as electron donor. CuL₂ is also known as precursor for photo-induced metal deposition [7].

2. Experimental

The LIBWE experiments were performed using a pulsed Ytterbium fiber laser of 1064 nm center wavelength and with a pulse duration of 25 ns (YLPM series, IPG Laser GmbH). For all experiments presented in this work the pulse repetition rate has been set to 100 kHz. All results presented here have been obtained using soda lime glasses as a substrate.

The soda lime specimens were cleaned with ethanol prior to the experiments (the label “untreated” will be used in the following for these substrates). For a second set of experiments soda lime glasses were treated with a dimethyldichlorosilane ((CH₃)₂SiCl₂) solution in toluene. As a consequence large parts of the surface will be covered with CH₃-groups. This leads to more hydrophobic and less polar surfaces compared to those of untreated soda lime glass. The measured contact angle of the surface for H₂O increases from 29° to 92° due to the silanization. For results obtained on these substrates the label “silanized” will be used in the following.

Line structures have been ablated using a galvo-scanner to control the scanning pattern, the lateral velocity of the laser beam and the number of passes. The ablated structures have been investigated by using a confocal laser scanning microscope (LSM). Quantitative information about the ablated depth per laser pulse could be inferred from the topographical data. The absorbance of CuSO₄ was 7.5, for CuL₂ 0.4. For both solutions the concentration of CuSO₄ was chosen to be very close to saturation. For the experiments with CuSO₄ the fluence of the laser beam was 4.95 J/cm² and a scan velocity of 20 mm/s was chosen. The corresponding values for the CuL₂ experiments were 7.1 J/cm² and 1 mm/s velocity. These settings were chosen such that the ablation per pulse remained rather weak to be able to monitor
differences from one pass to another. To ensure that all observed effects in the LIBWE experiments are due to the aqueous CuSO$_4$ and CuL$_2$ absorber liquids, control experiments have been done on untreated and silanized soda lime glass with pure H$_2$O as liquid. In neither of the two cases ablation effects have been observed.

3. Results
The ablation model for CuSO$_4$ and CuL$_2$ on untreated substrates has been discussed in detail in [5]. To briefly summarize, it is assumed that for CuSO$_4$, the energy of the laser pulse is absorbed by Cu$^{2+}$ ions adsorbed at the untreated and therefore polar substrate. For CuL$_2$ Cu$^0$ clusters in the solution are likely to be formed in a first step due to laser irradiation. These Cu clusters are then adsorbed on the glass substrate and act as absorber of subsequent laser pulses in a second step (see [5] for details). As also shown in [5] for CuSO$_4$, the silanization delays the onset of ablation. The reason for this is that Cu$^{2+}$ cannot adsorb easily to the silanized substrate because it is apolar (due to the CH$_3$-groups) compared to the polar untreated substrate [5]. However, after a few number of passes all silanized sites seem to be removed such that the ablation is then similar to the ablation on an untreated surface.

Fig. 1a shows the ablation depth per single pulse on untreated (open circles) and on silanized (open squares) soda lime glass substrates for CuSO$_4$ as absorber liquid for 25 and more passes (i.e. after removal of the silanized sites). The horizontal dashed line indicates the average value from all data points shown Fig. 1a. In accordance with the model described in [5] the ablation per pulse remains more or less constant as a function of the passes and is similar for untreated and silanized substrates.

Fig. 1b shows the results of similar experiments using CuL$_2$ as absorber liquid. Note that the absolute depth values for CuSO$_4$ (Fig. 1a) and CuL$_2$ (Fig. 1b) cannot be compared because of the different experimental settings, e.g. the different absorbance values (see section 2). At first sight one would assume that the adsorption of the Cu$^0$ clusters on the surface is not strongly influenced by polar (untreated surface) or apolar (silanized surface) groups. Therefore ablation is expected to be similar for both types of substrates. However, the data shown in Fig. 1b indicates the opposite. First, the ablation depth per pulse is about a factor 4.5 higher for the silanized compared to the untreated substrate. The ablation per pulse for the untreated substrate is more or less constant as a function of the number of passes, whereas for the silanized substrate the depth of ablation per pulse clearly decreases with the number of passes. This decrease let us again suppose that the silanized sites are removed after several ten or hundred passes. From the current data it is however not clear what the reason for the enhanced ablation for the silanized surface is. Detailed studies on the topography for the onset of ablation by atomic force microscopy studies will shed more light on this and will be presented in detail.

References
Laser printing of organic semiconductor layer is a key step in the realization of organic thin film transistors. We investigated the effects of laser-induced forward transfer process on the modification of the organic layer properties, both electrical and morphological, and the influence of these modifications on the transistor performances. Polymer and small molecule materials have been tested to printed p-type and n-type transistors. Mobilities up to 0.04 cm²/V.s, threshold voltage V_t near 0 V and Ion/Ioff ratio up to 2.8×10⁵ have been reached.

1. Context
For many applications within the microelectronics industry, the challenge is no longer one of pitch size reduction. The most relevant keywords are now 'flexible', 'low cost' and 'large area'. In this context, the typical dimension of the elementary unit is of the order of a few microns (3 to 50µm). The Laser-Induced Forward Transfer (LIFT) process appears a relevant technology for the localized deposition of organic and inorganic materials under liquid or solid format, and then the electronic device manufacturing [1-6]. The basic component of such device is the organic thin film transistor (OTFT) and this study is dedicated to characterization of the LIFT process ability to transfer the organic semiconductor (OSC) layer for the OTFT printing.

2. Materials and setups
p-type and n-type OSCs have been printed for the realization of bottom gate OTFTs. The main p-type materials investigated are copper phthalocyanine (CuPc), poly(3,3‴-didodecyl quaterthiophene) (PQT-12) for polymers and distyryl-quaterthiophene (DS4T) and Bis(2-phenylethynyl) end-substituted terthiophene (diPhAc-3T) as small molecules. Copper hexadecafluorophthalocyanine (F₁₆CuPc) material has also been printed as n-type material. The laser was a 50 ps Nd:YAG source (continuum leopard SS-10-SV) operating at 355 nm and the experiments were performed at room temperature and atmospheric or low pressure of air. LIFT principle has been described elsewhere [7, 8]. The donor was a suprasil substrate on which an OSC layer has been deposited by spin coating or thermal evaporation. The receiver substrate was based on a silicon (Si) wafer oxidized by a 300 nm thick layer of silicon dioxide (SiO₂) (Ci of 12 nF/cm²) and used as gate and dielectric in OTFT devices, respectively. Source drain electrodes were gold thermally evaporated or LIFT-printed silver nanoparticle inks. A square mask (300×300 µm²) was used to select a homogeneous part of the beam and image it on the donor thin layer using a converging lens. The accurate positioning of the sample was achieved using micrometric translation (x, y and z) stages and controlled by imaging the laser spot with a CCD camera. The wafer surface was cleaned by successive immersions with an ultrasonic agitation in acetone, tetrahydrofuran and then ethanol, subsequent rinsing and then blow-drying with an argon stream before use. Top contact (TC) OTFT devices were fabricated and immediately characterized in ambient conditions without precautionary measures being taken to exclude ambient light or atmospheric oxygen. Current-Voltage characteristics were obtained with a Hewlett-Packard 4140B pico-amperemeter DC voltage source under Labview® environment. All the measurements were performed at room temperature under ambient atmosphere. The field effect mobility μ was extracted from the transfer characteristics in the saturation regime. The drain-source current (I_D) in the saturation regime is governed by the following equation:

\[ (I_D)_{sat} = \frac{W}{2L} \frac{C_i \mu (V_G-V_t)^2}{2} \]

where C_i is the capacitance per unit area of the gate insulator layer, V_G is the gate voltage, V_t is the threshold voltage, and \( \mu \) is the field-effect mobility.

The morphology and the thickness of the deposited structures were investigated using optical (Zeiss Axiotech), scanning electronic (JEOL 6390), and atomic force (PSIA XE-100) microscopes.

3. Results and discussions
3.1. Morphological properties
The effects of LIFT process on film morphological properties have been investigated. Some OSC materials, as DS4T or PQT, are very sensitive to laser irradiation and the printed pixels are strongly damaged and generated a lot of debris. A dynamic Release layer (DRL) has been used to prevent this effect [9]. The triazene polymer (TP) DRL is spin coated on
the suprasil substrate before the deposition of the OSC layer. Then, the laser energy is absorbed by the DRL and converted in mechanical energy to push the OSC pixel toward the receiver substrate. Both DS4T and PQT-12 have been printed without damage with this approach. Other material, CuPc and F16CuPc are less sensitive to laser irradiation, and they have been printed without DRL. At last, the efficient cohesion of diPhAc-3T vacuum vaporized thin films induced by a 3-dimensional growth offers an exceptional high physical resistance to laser pulse. The high intermolecular interaction involved in such growth mechanism makes thin films less sensitive to the mechanical damages induced by the laser. Due to its optical properties, the use of a protecting layer deposited on the donor substrate prior the diPhAc-3T active layer to trap the incident radiation during the LIFT was not required. Whatever the OSC material, the laser fluence must be minimized to reduce the mechanical effects during transfer process and then to limit the risk of material modifications. Reduction of ambient pressure and smart beam shaping, beam profile with over intensities at the edges, allow a significant decrease of the minimum fluence required to print OSC pixels.

3.2. Electrical properties

The average mobility for CuPc based OTFT in top contact configuration was 8.10⁻² cm²/V.s [1]. The threshold voltage and the On/Off drain current ratio were 20 and 400 respectively. Similar results have been obtained with the n-type material F₁₆CuPc. Experiments have also been performed by printing PQT on Au photolithographically-patterned test-structures on doped silicon wafer. The electrical characteristics were a mobility of 2.4×10⁻² cm²/V.s and I_on/I_off ratio of 10. For comparison, the measured performances of the inkjet-printed transistors in the same configuration were: μ= 8×10⁻⁴ cm²/V.s, threshold voltage V_on, and I_on/I_off = 10². So, a lower I_on/I_off ratio and a higher mobility are observed for laser-printed OTFTs. The lower current ratio could be attributed to a degradation of the dielectric - semiconductor interface induced by the mechanical effect during the printing process.

Reproducible characteristics were obtained from different OTFTs prepared using DS4T pixels printed with TP as DRL [10]. Furthermore, with a mobility up to 0.02 cm²/V.s, a V_threshold near 0 V and an I_on/I_off ratio up to 3.10³, TC-OTFTs possess mobility values comparable to OTFTs prepared using DS4T vacuum vaporized layer at T_sub =30 °C [11]. The performance characteristics were highly consistent and reproducible with little transistor-to-transistor variation. Moreover, stability tests performed over 100 days haven’t shown any significant losses of performances. High and reproducible performances have also been been obtained with LIFT-printed diPhAc-3T pixel-based TC-OTFTs. Mobility up to 0.04 cm²/V.s, threshold voltage V_threshold near 0 V and I_on/I_off ratio up to 2.8×10² are characteristics highly comparable to OTFTs prepared using diPhAc-3T vacuum evaporated layer at T_sub =30 °C [12]. At V_G = 0 V, a low off-state current (I_off) was observed in the output characteristic giving rise to a high I_on/I_off ratio thereby revealing the absence of charges in the conducting channel. Additionally, a high mobility value and a low threshold voltage revealed the high structural cohesion of the pixels associated to a low density of trap states at the diPhAc-3T/dielectric interface. Such electrical data are directly correlated to lack of modification of the morphological properties observed by AFM and SEM. As for DS4T, OTFTs based on diPhAc-3T pixels printed by LIFT were stored over 100 days in the dark under ambient conditions and no decrease of the device performances was observed.

4. Conclusion

This study demonstrates that high performing OTFT devices can be fabricated using the LIFT technique. Process optimization allows the reduction of the material damages induced by the photochemical, thermal and mechanical effects potentially induced by the laser irradiation. The use of a DRL and the lowering of printing fluence are of prime importance. Mobilities higher than few 10⁻² cm²/V.s, threshold voltage V_threshold near 0 V and I_on/I_off ratio of 10³ have been reached. These performances are similar to those obtained by vacuum vaporization with the same materials and often higher than performances obtained with inkjet printing.

5. Acknowledgments

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References

Graphene is the most recent obtained allotrope of carbon. It differs from fullerenes and nanotubes in that it is a two-dimensional crystal. Graphene gained much attention from researchers due to its unique physical properties which can be used in various applications. This material has semiconductor features; it is mechanically strong and has high thermal conductivity at room temperature. There is still a lack of graphene production techniques, which are easily reproducible and contain minimum of hazardous materials. We present a graphene production method based on laser irradiation induced graphite oxide reduction. Handling of the laser beam enables precise writing of micro-channels which can be used in electronics as contacts or as a part of heat removing system. Experiments were conducted in argon atmosphere using 1064 nm, 532 nm and 355 nm radiation of the picosecond laser. Irradiated samples were analyzed by means of optical and scanning electron microscopy and Raman spectroscopy.

1. Introduction
Graphene can be produced by mechanical exfoliation, chemical exfoliation, chemical synthesis, pyrolysis, epitaxial growth, CVD and other methods [1]. There is still a need for novel graphene production methods which are suitable for mass production and can avoid usage of harmful chemical materials. Chemical, thermal and light reduction methods are implied for graphite oxide (GO) reduction. Recently several methods of producing graphene based on laser-induced GO reduction have been described [2-6]. We present results of our research on localized reduction of GO into graphene using picosecond laser radiation.

2. Experimental setup and samples
Graphite oxide was synthesized using the modified Hummers – Otieman method from a graphite precursor. The Congo Red (CR) dye was used as an additive [7]. Graphite oxide preserves the layered structure of its predecessor graphite. To arrange individual graphene sheets regularly and form larger graphene layers functional reagents are used. Such agents can be large organic molecules with certain functional groups that react with the graphene or graphite oxide nanostructures existing functional groups, joining GO sheets into larger moieties.

Sonicated GO-CR suspensions were used to produce GO/CR nanocomposite coatings. The coatings with the thickness of 1200 nm were prepared on the polycarbonate membrane filters via slow filtration into alkaline media. Obtained coatings were flexible in a wet ambient. Mechanical properties of the coatings were dependent on the GO to CR ratio. The samples were treated using a picosecond laser (Atlantic, 10 ps, 100 kHz, Ekspla) working at 1064 nm, 532 nm and 355 nm wavelength. Experimental setup Fig. 1 included the laser, electro-optical shutter, beam expander and galvanometric scanner with a focusing objective (F = 80-170 mm). During the tests, the average laser power was varied from 5 mW to 50 mW. The scanning speed was changed in the range of 5 – 100 mm/s. The sample was placed inside a chamber with controllable ambient.

Figure 1: Experimental setup scheme a) SEM picture of the laser scribed lines in GO film b) Process parameters: λ-1064 nm, 50 µJ irradiation dose, laser treatment in nitrogen atmosphere; Sample: aqueous GO suspension, concentration. 1.5*10^-4 g/ml; filtered to 0.1 M KOH, PC substrate (pore d=0.4 µm) doped with Congo Red dye.
The picosecond laser irradiated samples were analyzed using Raman spectroscopy Fig. 2. The measurements were performed with 632.8 nm excitation (He-Ne laser) by using the confocal Raman spectrometer/microscope LabRam HR800 (Horiba Jobin Yvon) equipped with a grating containing 600 grooves/mm and a liquid nitrogen cooled CCD camera down to -132°C working temperature. Laser power at the sample was restricted to 1 mW and the laser beam was focused to ~ 2 µm diameter spot on the surface. Spectra were taken with 50x objective lens. The overall integration time was 100 s. Raman spectra were captured from the center of laser scribed lines and untreated area of GO film for comparison.

![Figure 2: 1-Measured Raman spectrum of laser treated GO, 2 D band Lorentz fit, 3 - G band Lorentz fit, 4 - D’ band Lorentz fit, 5- 2D band Lorentz fit, 6 – Peak sum; Process parameters are same as in Fig. 1.](image)

Use of low laser irradiation power (5-20 mW) did not initiate any significant changes in the Raman spectra compared to the spectrum of the untreated GO area. Use of 30-50 mW optical power caused a significant increase in the intensity of the 2D peak, indicating formation of graphene phase. On the other hand, a minor rise of intensity and narrowing of the D line were also observed. It can be explained by structural surface defects, which can be created by evaporating of water molecules and carboxyl, hydroxyl and epoxide groups [8].

3. Conclusion

Irradiation of GO films with the picosecond laser induced significant changes in material properties. Raman spectra changes indicated formation of the few-layer graphene. The optimal Congo Red concentration corresponded to the situation when CR molecules preferentially were located on edges of GO sheets and joined them together, creating larger nanoplates. Simulation revealed that the temperature above 1000°C, which is necessary to remove most of carboxyl, hydroxyl and epoxy groups from GO, was achieved under optimal laser beam scanning conditions.

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References

SCIBING OF SAPPHIRE WAFERS BY USING PICOSECOND LASER IRRADIATION AT 355 NM

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Scribing of sapphire wafers was performed by using the picosecond laser radiation at 355 nm wavelength. The Gaussian laser beam was tightly focused inside the transparent sample until nonlinear absorption was reached. The internal heating induced stresses in the region of a focal spot of the beam. The cracks occurred in the sample along the scanning direction. The force was applied to the wafer and its singulation along the fracture direction was achieved. On the basis of the scribing conditions obtained from the experiments, a three-dimensional thermal stress analysis was conducted by the finite element method. The scribing condition was estimated from the maximum tensile and compressive stresses and the maximum temperature.

1. Introduction

Single crystal sapphire (Al₂O₃) offers superior physical, chemical and optical properties, which make it an excellent material for applications, such as high-speed integrated circuit chips, thin-film substrates, and various electronic and mechanical components [1, 2, 3]. Sapphire is mechanically and chemically difficult to machine because of its high hardness [4] and chemical stability [5]. Laser processing has been proposed as a potential machining method of sapphire. The interaction of laser pulses with sapphire material has been investigated for many years [6, 7, 8]. However, the surface scribing of wafers contaminates the substrate. Intra-volume laser dicing of sapphire is a promising technique. In this work, the intra-volume scribing of sapphire wafers with picosecond laser pulses was investigated under various conditions of pulse energies and distances between laser pulses at 355 nm wavelength. On the basis of the experimental results, a three-dimensional thermal stress analysis was conducted by the finite element method for the purpose of theoretical clarification of the factors ruling the scribing conditions and the crack depth.

2. Experimental

Experimental setup for the sapphire wafer scribing is shown in "Fig. 1a". The picosecond laser PL10100 (Ekspla Ltd.) with the pulse energy up to 26 µJ at 355 nm wavelength was used in the experiments. The pulse duration was 10 ps (FWHM) at the repetition rate of 50 kHz.

![Figure 1: (a) Principal scheme of the intra-volume scribing of a sapphire wafer. (b) Optical microscope image of the laser scribed and singulated sapphire wafer.](image)

The sapphire wafer was scribed by using laser pulses, and then external force was applied to singulate the wafer. The image of cross section of scribed sapphire is given in "Fig. 1b".

3. Modelling

On the basis of the scribing conditions obtained in the experiments, a three-dimensional transient thermal stress analysis was conducted by the finite element method using the COMSOL Multiphysics software. The Gaussian laser beam with the intensity profile \( I_{x,y,z,t} \) was focused inside the sapphire wafer:

\[
I_{x,y,z,t} = I_0 \frac{w_0^2}{w^2} \frac{z}{w^2} e^{-\frac{x^2+y^2}{w^2}} e^{-\frac{z^2}{z_R^2}},
\]

where \( x \) and \( y \) are the transverse coordinates, \( z \) is the longitudinal coordinate, \( t \) is the time, \( I_0 \) is intensity at the centre of the beam, \( w_0 \) is the beam waist \((1/e^2)\), \( w = w_0 \sqrt{1 + \frac{z^2}{z_R^2}} \) is the beam radius along the longitudinal direction, \( z_R = \pi w_0^2 n / \lambda \) is the Rayleigh length, \( \lambda \) is the wavelength, \( n \) is refractive index, \( \tau \) is the pulse duration (FWHM). The attenuation of the beam or absorbed laser power per volume of intensity \( I \) is [9]:

\[
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\]

MO-3A-5-RO
\[ \frac{dl}{dz} = -\alpha l - \beta \beta^2, \]

where \(\alpha\) is the loss coefficient due to absorption and scattering, and \(\beta\) is the two-photon absorption coefficient. In the case of one- and two-photon absorbing media, the intensity transmitted through the sample can be described as [10]:

\[ I(x, y, z, t) = \frac{1 - R}{1 + \beta (1 - R)} I(x, y, 0, t) e^{-\alpha z}, \]

where \(R\) is the reflectivity of the sample. The laser power absorbed by material is finally converted to heat. The time-dependent temperature distribution at the target depth \(T(x, y, z, t)\) is governed by the heat flow equation appropriate to many experimental situations [11]:

\[ \rho C P \frac{\partial T}{\partial t} = \kappa \frac{\partial^2 T}{\partial x^2} + q, \]

where \(\rho\) is the density, \(C_P\) is the specific heat, \(\kappa\) is the thermal conductivity, \(q = -dl/dz\) is the absorbed power per volume. The equation governing the thermal stresses due to the laser pulse heating can be written through stress-strain relations [12]:

\[ \sigma = D \varepsilon_m, \]

where \(\sigma\) is the stress vector, \(D\) is the elasticity matrix, \(\varepsilon_m = \varepsilon - \varepsilon_T\) is the mechanical strain vector, \(\varepsilon\) and \(\varepsilon_T\) are total and thermal strain vectors, respectively. The temperature distribution and the stress of the sapphire wafer are given in Fig. 2.

4. Conclusions

In conclusion, the three-dimensional thermal stress analysis based on the experimental results including the crack depth, the crack profile and the scribing conditions was conducted by the finite element method. The crack depth depends on the maximum tensile and compressive stress field present immediately under the crack. A qualitative agreement was found in crack formation between the experimental data and simulation results.

References

UV PICOSECOND-LASER INDUCED BULK MODIFICATIONS AND LUMINESCENCE IN SINGLE-CRYSTAL DIAMOND

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Bulk laser-graphitized microstructures have been fabricated in type IIa single-crystal 1.2-mm-thick diamond plates by UV laser irradiation with 10-ps pulses at λ = 355 nm wavelength. It is found that the crystallographic-plane-dependent character of structural modifications in the bulk is influenced by the laser wavelength and the direction of the laser beam incidence along a given crystallographic direction (⟨100⟩ or ⟨110⟩) in the samples. High-order Stokes Raman lasing is observed during UV laser irradiation and bulk modifications of single-crystal diamond.

Recently we have demonstrated high-rate bulk modification and microstructuring of type IIa single-crystal mm-thick diamond plates using a picosecond MOPA laser system with 10-ps pulses at λ = 532 nm wavelength [1]. The fundamental result of our studies (reported in [1]) is related to the findings of crystallographic-plane-dependent character of bulk modifications and the 3H luminescence which are of great interest for understanding the mechanisms of ultrafast phase transitions and the 3H center formation during ps-laser irradiation and of importance for applications dealing with laser microstructuring in the bulk of single crystals to be controlled by the strength anisotropy of diamond.

In this paper, we used the 3rd laser harmonic (λ = 355 nm) of the picosecond MOPA system [2,3] to study the bulk modifications and luminescence induced in single-crystal diamond by UV ps-laser irradiation.

The type IIa CVD single crystal diamond plates of 6.0x1.7x1.2 mm size, with mechanically polished {100} growth faces and {110} side faces, nitrogen content [N] < 1 ppm, were used as the samples for UV laser microstructuring. The UV laser beam was focused onto the rear side of the diamond plates; the pulse energy was varied from 0.1 μJ to 6 μJ, and the pulse repetition rate – from 10 to 50 kHz. A video imaging system was applied for real-time observation of the growth of a laser-modified region in the bulk of diamond, from the rear side towards the front side of the plates, in the course of multipulse laser irradiation [1]. In addition, UV ps-laser induced photoluminescence (PL) spectra over the range of 350-1000 nm were recorded during laser irradiation; the PL setup provided measurements perpendicularly to the laser beam through a polished side face of the sample. The microstructural properties of the UV laser-modified regions were examined using micro-Raman and photoluminescence spectroscopy at the 488 nm excitation wavelength.

Using the developed techniques, bulk microstructures have been fabricated in 1.2-mm-thick single-crystal diamond plates at different pulse energies and pulse repetition rates of the UV ps-laser. The crystallographic-plane-dependent structural modifications in the bulk are clearly pronounced to occur along {111} planes during irradiation with UV laser pulses. It is found that changing the direction of incidence of the laser beam (parallel to the crystal ⟨100⟩ direction or to the ⟨110⟩ direction) strongly influences the microstructure formation in the bulk of diamond. Possible mechanisms of the observed behavior and its dependence on the laser wavelength and the direction of incidence will be discussed. Results of microstructural studies of the laser-modified diamond, 3H luminescence will be also presented and discussed.

Photoluminescence spectra recorded in the course of UV laser irradiation have enabled important data on the ps-laser induced processes in the bulk of diamond to be obtained. The laser-induced PL due to the nitrogen-vacancy (NV) defects, NV luminescence, is observed at wavelengths of 575-750 nm [1]. This makes the UV laser beam ‘visible’ as well as its reflections from the ‘laser-graphitized’ {111} planes in the bulk of diamond, that evidences the formation of an optically sharp boundary between original and laser-modified material. In addition to the NV luminescence, stimulated Raman scattering (SRS) is generated in the diamond crystals under UV ps-laser irradiation. With increasing pulse energy the SRS lasing has been observed at the 1st Stokes, 2nd Stokes, and 3rd Stokes wavelengths – λ1S = 372.6 nm, λ2S = 392 nm, λ3S = 413.7 nm, respectively. It is demonstrated that the formation of a bulk microstructure leads to dramatic changes in the PL spectra and SRS lasing. The obtained results are important for further study of the SRS in diamond and development of novel Raman laser devices (see ref. [4]) based on high-quality single crystals.

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References
Femtosecond fiber-based MOPA – current status and future prospects for industrial applications in cold-ablation micromachining

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There are emerging industrial requests for precision micromachining laser systems with both high-energy ultrashort pulses and high average power to increase the system’s productivity. Based on the MOPA architecture of the established and industrially-proven Duetto picosecond product family, Time-Bandwidth has developed a fiber-based, high-power femtosecond laser system addressing these industrial requests. Along with the sufficient pulse energy for micromachining, the system offers pulse repetition rates of up to 8 MHz to efficiently use the achievable average power. The system was developed within the framework of the EU-funded project “LIFT” which addresses high-power fiber technology for industrial applications. Cutting-edge fiber technology should allow for scaling of advanced beam deliver to multipoint multi-scanner systems or line scanners for large area production.

Here we present our current results with a MOPA designed for up to 200W of average power based on a large-mode area fiber-based power amplifier, and discuss system parameters and key-requirements for ultrafast micromachining applications with high productivity.
MULTI-STAGE YTTERBIUM FIBER-AMPLIFIER SEEDED BY A GAIN-SWITCHED LASER-DIODE

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We followed the interesting approach of combining a gain-switched laser diode with a ytterbium doped fiber amplifier (YDFA) for the generation of energetic picosecond pulses. We demonstrated all-fiber direct amplification of 11 picosecond pulses from a gain-switched laser diode at 1064nm. The diode was driven at a repetition rate of 46.3MHz and delivered 12µW of fiber-coupled average output power. For the low output pulse energy of few 100fJ we have designed a multi-stage core pumped pre-amplifier based on single clad Yb-doped fibers in order to keep the contribution of undesired amplified spontaneous emission as low as possible. After the pre-amplifier we reduced the 46.3MHz repetition rate to 1MHz using a fiber coupled pulse-picker. The final amplification was done with a cladding pumped Yb-doped large mode area fiber and a subsequent Yb-doped rod-type fiber. With our setup we reached pulse energies of >5.6µJ and peak powers of >0.5MW.

1. Introduction

Semiconductor gain-switched laser diodes with direct fiber amplification are compact, reliable and cost-effective sources of picosecond pulses with pulse energies up to several µJ and tunable repetition rates from pulse-on demand to GHz. Shorter pulses with higher peak powers than currently available from such systems are desirable for certain applications, e.g. in material processing the efficiency and quality of metal ablation is significantly improved [1]. Gain-switched laser diodes allow low-jitter electronic triggering of laser pulses. This is a very attractive feature for many applications such as material processing [2] or nonlinear wave-mixing [3]. The drawback of using gain-switched laser diodes as seed for amplification is the weak output pulse energy in the order of few 100fJ [4]. However, fiber amplifiers allow low-noise amplification of weak signals and are thus ideally suited to amplify the weak pulses from gain-switched laser diodes [5].

2. Experimental Setup

The experimental setup of our fiber laser system is sketched in Fig. 1. The gain-switched laser-diode delivered 12µW of average fiber coupled optical output. The diode delivered un-polarized picosecond pulses at a wavelength of 1063.3nm, with 32ps temporal width (FWHM) and at a repetition rate of 46.3MHz. By using a dispersion compensating element in the first amplification stage the pulses were temporally compressed by a factor of about three to 11ps (FWHM). After the first stage the signal passed an inline-polarizer and the subsequent amplification was based on polarization maintaining optical components and fibers. After the second amplification stage, the repetition rate was reduced from 46.3MHz to 1MHz for the final amplification. The core diameters of the optical fibers were gradually increased for the consecutive amplification stages up to 70µm. This prevented undesired non-linear effects or even damage of the fibers due to the high pulse peak powers. The final amplification was done by using a large mode area (LMA) fiber with 30µm and a rod-type fiber of 70µm core diameter, both optically pumped at a wavelength of 976nm in counter-pump configuration.

Fig. 1 Experimental setup of the five-stage fiber amplifier seeded by a gain-switched laser diode.
3. Results
Each YDFA-stage was optimized for high gain and low ASE contribution.
The first YDFA-stage was gain-limited due to occurrence of spontaneous lasing at a wavelength around the Ytterbium
gain maximum at 1030nm. We assume that the spontaneous lasing happened because of weak back-reflections around
1030nm in the fiber-optical elements. Depending on the chosen polarization plane, multiple pulses separated by few
picoseconds or single pulses were observed after the in-line polarizer. Thus, the polarization controllers shown in Fig. 1
were adjusted to get single pulses after linear polarization. A dispersion compensating element was incorporated in the
first amplification stage (Fig. 2b). The temporal compression by the dispersion compensating element was about a
factor of 3 resulting in a temporally compressed laser pulse of about 11ps FWHM.

Fig. 2 Spectral and temporal amplification characteristics of our multi-stage fiber amplifier.
a) Spectra recorded with an optical spectrum analyser show spectral broadening during the amplification
process. b) Autocorrelation-traces show the temporal pulse width evolution of the laser pulses during the
amplification process. After temporal compression in the 1st amplification stage, we observed no significant
change of the temporal pulse duration.

The second YDFA-stage was gain-limited by the occurrence of temporal pulse width broadening. After the second
YDFA-stage the repetition rate was reduced from 46.3MHz to 1MHz by using a pulse-picker. The achievable gain
while keeping short pulse duration of the third YDFA-stage was also gain-limited by the occurrence of pulse
broadening. For both stages we observed a rising peak at approximately 1217nm. This is in the wavelength region,
where a Raman-peak is expected to arise for such fibers. The fourth stage was gain-limited by the occurrence of
spontaneous lasing. We assume these came from weak back-reflections of the angle-cleaved LMA fiber-ends. In the
fifth (rod-type) YDFA-stage we achieved an average signal output power of 5.6W at a repetition rate of 1MHz. This
corresponds to a pulse energy of 5.6µJ and a peak power of >0.5MW. The gain in the fifth YDFA-stage was limited by
available pump power.
The overall amplification stages achieved gain was 73dB. The pulse shapes did not change significantly throughout the
amplification process as indicated by the auto-correlation traces shown in the Fig. 2b.

4. Summary
The output of a gain-switched laser diode was compressed by a factor of approximately 3 by using a dispersive optical
element to a pulse-duration of 11 ps. We have demonstrated the amplification of the weak pulses (0.26pJ) by 73dB to an
output pulse energy of >5.6µJ. After optimizing the multi-stage fiber amplifier, no significant temporal pulse
broadening was observed during the amplification process. We estimated the peak power to be >0.5MW. To the best of
our knowledge, we achieved the shortest pulse duration and highest peak power with ytterbium fiber based direct
amplification of laser pulses generated by a gain-switched laser diode that is driven at MHz repetition rates.

References
PASSIVE PHASE LOCKING OF NANOSECOND PULSED FIBER AMPLIFIERS BY ALL-OPTICAL FEEDBACK LOOP

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We demonstrate a passive coherent beam combining of two nanosecond amplifiers using by all-optic feedback loop. The total combined peak power is 25.3W with 9.7ns pulse width and 2.023MHz pulse repetition frequency. The visibility of far-field coherent patterns is more than 71%. The dynamics of passive phase locking is studied and the establish time of phase locking in all-optic feedback loop is calculated.

1. Introduction
High power pulsed fiber sources with diffraction-limited beam quality have important applications in many aspects, such as material processing, remote sensing and laser radar, and so on. However, producing high output power from one single fiber laser is prevented by thermal effects, facet damage, and deleterious nonlinearities. Fortunately, coherent beam combination (CBC) of fiber amplifiers has been demonstrated to be a promising technique for scaling the output power with good beam quality [1]. Most of previous works concerning CBC have been performed in a Continuous wave regime, and kilowatt level output power was demonstrated [2]. It is worth noticing that some literatures demonstrated active CBC of pulsed fiber laser [3]. Su et al. reported active CBC of two fiber amplifiers with 8ns pulse width and 215.8W average power [4]. Passive CBC of fiber amplifiers array using by all-optical feedback loop has great potentialities in power scaling and does not need a complex electronic servo system[5]. J. Guillot demonstrated that the recovery time of co-phasing of the all-optic feedback loop after an environmental perturbation takes only a few cavity round trips. The fast co-phasing dynamics of all-optic feedback loop indicated that it can also deal with passive CBC of short nanosecond pulses. Up to now, the dynamics of a passively combined system have been theoretical approached and numerical simulated by some previous papers. However, the establish mechanism is still an interested issue for passive CBC.

2. Experiment setups
The experimental arrangement is depicted in Figure 1. A CW laser from a 1064nm laser diode is modulated to a pulsed laser by a commercial electro-optic amplitude modulator (EOAM). The ratio frequency signal for driving the EOAM is supplied by an arbitrary waveform generator (AWG). Two preamplifiers A1 and A2 are employed to amplify the pulsed laser. Then the laser beam is fed into two channels by a 50/50 coupler. Both of the two main amplifiers (A3) boost the average power of the pulsed laser to about 250mW. The output beams of the two channels are space arranged via two collimators. The diameter of the laser beam output from the collimator is 4mm and the distance between the two beams is 11mm. One part of the output beams are reflected by a sampler with 10% reflectivity and coupled into a polarization maintaining single mode feedback fiber (PMSMF) by a lens with a 400mm focal length. In the feedback loop, the average power of feedback pulsed signal is amplified by a feedback amplifier (A0) to about 3mW. The feedback pulsed signal is fed into the EOAM by a coupler and the all-optic feedback loop is established. 90% power of the output beams pass the sampler as output signal and is detected by a charge-coupled-device (CCD) camera for far-field interference patterns, a photodetector (PD) for pulse shapes, and a power meter for combined power. All of amplifiers are polarization maintaining single mode amplifiers.

Figure 1: The experimental arrangement (AC: angle cleave; PD: photodetector; CO: collimator; RF: ratio frequency)
3. Results and discussions

Once our system is in close loop, the phase of two nanosecond fiber amplifiers will be locked steadily in a very short time. The total combined average power is 507mW. Figure 2(b) shows the visually pleasing coherent patterns of the in-phase mode with 9.7ns pulse width and 2.023MHz PRF. The visibility of the patterns is up to 71% where the visibility is defined by the formula \( \frac{I_{\text{max}} - I_{\text{min}}}{I_{\text{max}} + I_{\text{min}}} \), where \( I_{\text{max}} \) and \( I_{\text{min}} \) are the maximum optic intensity and the adjacent minimum on the intensity pattern respectively. The temporal characters of the output beams before and after combined are shown in Figure 4(c) and (d). It is obvious that the pulse shape of the combined beam is almost the same as each channel.

![Far-field patterns of the out-phase mode](image1)

![Far-field patterns of the in-phase mode](image2)

In conclusion, we demonstrate a CBC of two nanosecond amplifiers using all-optic feedback loop. The total output average power is 507mW with 9.7ns pulse width and 2.023MHz PRF. The visibility of far-field coherent patterns is up to 71%. And we study the dynamics of passive CBC and calculate the establish time of phase locking in all-optic feedback loop. The fast phasing time indicates that all-optic feedback loop have a pleasing potentiality in passive CBC of sub-nanosecond domain. And take the performance of all-optic feedback loop in CW CBC into account, passively phase locking of pulsed fiber amplifiers with higher output power and more channels will be realized. These will be demonstrated in our following study.

References


Gain-switched laser diode seeded fiber amplifiers for nonlinear frequency conversion

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Based on the amplification of gain-switched laser diodes around 1550 nm, we have designed an all-fiber laser source delivering 40 ps pulses with a pulse energy of 0.5 µJ at 1 MHz repetition rate; the laser pulses are close to bandwidth limited. The system required a careful design to effectively reduce the amplified spontaneous emission and allow power scaling with negligible spectral and temporal distortions. We characterized the timing jitter between two electronically synchronized seed diodes and we explored possible frequency mixing scenarios based on nonlinear frequency mixing of two different, electronically synchronized seed diodes.

1. Multi-stage Er-doped fiber amplifier

Gain-switched semiconductor laser diodes are very attractive sources of picosecond pulses [1, 2] because they are compact, stable and provide tunable repetition rates from pulse-on-demand up to hundreds of megahertz. They are a good alternative to picosecond mode-locked lasers, which are more expensive, less robust and require complex long-cavity designs or pulse pickers to reach repetition rates below 10 MHz. The pulse energy of gain-switched laser diodes is, however, typically only of the order of a few tens of picowatts. As a consequence, the pulses need to be amplified by several tens of dBs, in order to reach energy levels in the microjoule range nowadays available from mode-locked lasers.

In this paper we present a picosecond fiber laser source with a 1-MHz repetition rate based on an Er-doped fiber amplifier seeded by a gain-switched laser diode. The laser diode provides 40-ps pulses with 2.15 pJ of pulse energy and 2.15 µW of average power. The three-stage amplifier consists of a two-stage core-pumped Er-doped fiber preamplifier, followed by a commercial ErYb-doped double-clad soft-glass fiber amplifier. The first stage of the preamplifier provides 26-dB amplification. After the second stage of the preamplifier we reach a total output power of 14 nW (14 nJ pulse energy), which corresponds to a total gain of 38 dB. Since the signal spectrum has a spectral width of only 0.1 nm FWHM and can be well distinguished from the ASE spectrum, the amount of ASE can be estimated by calibrating the optical spectrum with the total amount of measured output power. With the use of in-line fiber filters we achieve to effectively suppress the ASE (26 dB signal-to-ASE extinction ratio). In fact, the power of the gain-switched laser diode is so low that careful design and optimization of filters and fiber dimensions are required to significantly amplify the signal without strong onset of ASE [3,4]. The output spectrum in logarithmic scale is shown in Fig.1 (a).

![Optical spectrum at the output of the second stage of the preamplifier (14 nJ pulse energy)](image)

**Fig. 1** (a) Optical spectrum at the output of the second stage of the preamplifier (14 nJ pulse energy), which clearly shows the significant suppression of ASE even after 38 dB amplification. Proper filtering has reduced the ASE spectral width to only 3.3 nm, and the signal-to-ASE extinction ratio amounts to 26 dB. (b) Optical spectrum after the boost amplifier (0.5 µJ pulse energy). Even if the ASE has not been filtered in this stage, the signal-to-ASE extinction ratio is only 14 dB (which means that the signal amounts to 96% of the total output power).

The boost amplification stage is based on a commercial ErYb-doped double-clad soft-glass large-mode-area fiber amplifier module from Polar Laser Laboratories [5]. The system can deliver 0.5 W average signal power, which
corresponds to pulses of 0.5 µJ pulse energy and 11 kW peak power. The signal-to-ASE extinction ratio at the output of the boost amplifier amounts to 14 dB (signal corresponding to 96% of the total output power). The output spectrum in logarithmic scale is shown in Fig.1 (b). The signal-to-ASE ratio is comparable only to the most recent achievements in Yb-doped fiber amplifiers in an all-fiber configuration [1], and it has not been reported yet for an Er-doped amplifier at 1 MHz repetition rate. Furthermore, we succeeded to obtain a very narrow spectrum and almost transform-limited pulses. In Fig.2 (a) we report the spectrum in linear scale with a resolution of 0.02 nm, and we compare it with the spectrum of the seed. Spurious spectral components of the gain switched laser diode have been filtered out in the preamplifier and the spectrum presents a nice Gaussian profile with 0.1 nm FWHM spectral width after the boost amplifier. Amplification occurred without significant temporal distortions as well, as we can see in Fig.2 (b). The time-bandwidth product corresponds to 0.57, approaching the theoretical transform-limited value for a Gaussian pulses (0.44).

2. Nonlinear frequency mixing
The very low noise figure and narrow spectral width make of this system an extremely interesting picosecond laser source for nonlinear frequency mixing in crystals. In fact, in order to have efficient nonlinear frequency conversion at these power levels, it is extremely important that the spectrum lies well within the acceptance bandwidth of the nonlinear crystal. For this reason, special care has been taken to avoid spectral broadening due to the onset of saturation and nonlinear effects in the fibers.

In order to perform nonlinear frequency mixing other than second-harmonic generation, we also built a fiber preamplifier for a gain-switched laser diode at 1540 nm and 1064 nm. We electronically synchronized the two diodes, and we focused the two amplified beams into a periodically-poled Lithium Niobate crystal (PPLN) of appropriate poling period for sum-frequency generation at 629 nm. The maximum power extracted at 629 nm was only 400 µW when pumping with 50 mW at 1064 W and 20 mW at 1540 nm, which corresponds to only 0.5% conversion efficiency. To investigate the origins of such a low efficiency, we characterized the relative timing jitter between the two electronically synchronized seed diodes with a fast oscilloscope and with nonlinear cross-correlation techniques [6,7]. By using statistical analysis of the variations of the intensity temporal distribution we estimated the relative time jitter of 25 ps, which is comparable to the pulse length of the pump pulses (27 ps at 1540 nm and 39 ps at 1064 nm). This high relative timing jitter inevitably degrades the nonlinear conversion efficiency, but it can be reduced by optimization of the electronic synchronization process.

References
We present an all-fiber frequency-stabilized ring laser system with an integrated reference gas cell consisting of a hollow core fiber filled with acetylene. Through nonlinear absorption spectroscopy the laser frequency is stabilized to a specific absorption line of acetylene. Three different stabilization schemes are investigated and the minimum Allan deviation obtained after 100 s is $4.4 \times 10^{-11}$.

1. Introduction

Stabilized laser systems are used as frequency references, realization of the definition of the meter, in cold atom trapping, or for calibration of optical components to name but a few. In such laser systems the frequency is usually stabilized to a precisely known reference which may be an atomic, ionic, or molecular transition. In the C-band the Bureau Internationale des Poids et Mesures (BIPM) commends the use of acetylene at a pressure of $(3\pm2)$ Pa as a reference. At such low pressures one often employs multi-pass cavities to increase the effective absorption length well beyond the cavity length, thus, enhancing the signal-to-noise ratio. The observed line widths of the relevant acetylene transitions in linear absorption measurements are inhomogeneously broadened and depend on the ambient temperature (Doppler broadening). In order to have access to the narrower homogeneous line widths, thus increasing the accuracy with which the absolute frequency can be determined, one often uses nonlinear saturation spectroscopy. For telecommunication applications it would be desirable to realize a robust all-fiber frequency standard which is compatible with commercial fiber components. Specifically, such an all-fiber system would require a fiber-based absorption cell, which became possible with the advent of hollow core photonic band gap fibers (HCPCF). A number of groups have demonstrated stabilization of a fiber laser in combination with bulk gas cells; here, we present an all-fiber version of a frequency-stabilized laser system operating in the C band. We examine three different methods to stabilize the laser frequency to the nonlinear saturation dip of the P15 acetylene transition.

2. Results

The ring laser constructed can be tuned mode-hop free within a frequency range of about 1.3 GHz, limited only by the intra-cavity piezo actuator, as shown in Fig. 1. The width of the cavity mode was measured to <2 kHz and the ASE background is 65 dB below signal level. An integral part of all stabilization experiments is an all-fiber gas cell; details may be found in reference [1]. At room temperature the inhomogeneous line width is 466 MHz. The homogeneous line width is determined by pressure, transit time, and power broadening. Pressure broadening values are between 5.6 MHz/mbar and 10.7 MHz/mbar. Transit time broadening amounts to $(21.6\pm2.2)$ MHz for the HCPCF used. That is, for pressures smaller than a few mbar transit time broadening is the dominating mechanism. We fill the HCPCF with approximately 2 mbar as a compromise between strong enough absorption strength and low enough pressure broadening. To obtain a sufficiently large feedback signal we use a laser power of 200 mW which further broadens the line by about a factor of 1.5. The resulting homogeneous line width is measured to $(47\pm2)$ MHz.
In the following we investigate three different stabilization schemes. Specifically, we examine a classical pump-probe scheme with two counter-propagating beams, a reflected pump beam version of the latter, and the Pound-Drever-Hall scheme. The stabilized frequency is compared to an optical frequency comb (Menlo System FC1500) at METAS, which is referenced to a hydrogen maser. The comb measures absolute frequencies with an uncertainty of a few 100 Hz. To quantify the stability we extract the Allan deviation from the measured frequency versus time. Table 1 summarizes the results for the three different schemes. Without any additional measures we find that the S/N ratios are similar for all three schemes. While the lowest S/N of 40 is found for the reflected pump, the highest S/N of 180 is obtained for the Pound-Drever-Hall scheme. Further, the S/N ratio is limited by interferences from the absorption cell, the poor single-mode behavior of the HCPCF, and the small birefringence. Interferences can be mostly eliminated through dithering the HCPCF length. Consequently, the S/N ratio improves by almost two orders of magnitude (from 40 to 1700). Although we applied this measure only to the reflected pump scheme, it should be applicable to all three schemes. In the same way dithering the cavity length eliminates interferences, polarization scrambling should reduce the fluctuations due to the birefringence of the HCPCF. However, we find that dithering and polarization scrambling does not further improve the S/N ratio, it rather has the adverse effect.

<table>
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<td>None</td>
<td>180</td>
<td>$3 \times 10^{-10}$</td>
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Table 1: Summary of results.

References
HIGH POWER FIBER LASERS AND THEIR COHERENT BEAM COMBINATION

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Recent progress of fiber laser research at SIOM are given, including the thermal effects of kW level CW fiber laser, Compact all fiber 102 W picosecond MOPA fiber laser system with narrow spectral line-width and Diode pumped 1018nm Yb-doped double cladding fiber laser. kW level passive phase locking of four high power Yb doped fiber amplifier chain are also given.

Summary

Fiber lasers hold great promise for a wide range of applications because fiber lasers have high efficiency and exceptional beam quality. On the other-hand, fiber lasers are truly solid state with minimum of exposed optical interfaces, the high beam quality and 1 um wavelength makes it possible that the fiber laser can directly replace both diode and lamp pumped Nd:YAG lasers in many industry applications, the most important markets they will address are marking, micromachining, automotive and biomedical.

Fiber lasers up to 10kW output power are now on high technological level, fiber laser systems for industrial applications are now on the market. The development of these lasers is not only in the cw and long pulsed mode operation but also in the short ps pulse mode operation. It is no question that the diode pumped fiber lasers offer many advantages for well known reasons:

- High overall efficiency (20% - 30%)
- High life time (5000h to several tens of thousand hours)
- Lower energy consumption and less cooling
- More stable laser emission
- Less weight and volume, which is of special interest for making and scribing applications
- Less thermal load, which results in a higher beam quality

In this paper, recent progress of fiber laser research at SIOM are given as follows:

1. The thermal effects in kilowatts all-fiber MOPA fiber laser system is investigated, transverse and longitudinal temperature distribution in fiber laser have been calculated by solving the thermal conduction equations, three kinds of cooling apparatus were used to improve the heat conduct. 1.17 kW output operating at 1080nm was obtained with optical to optical conversion efficiency of 82.4% was demonstrated.
2. Compact all fiber 102 W picosecond MOPA fiber laser system with narrow spectral linewidth of 0.1nm was obtained with optical to optical efficiency of 62%.
3. Diode pumped 1018nm Yb-doped double cladding fiber laser is demonstrated with output power of 7.5W and pumping power of 59W.
4. Passive phase locking of four high power Yb doped fiber amplifier chain by using a ring cavity, each amplifier chain can reach about 250W output power, the maximum coherent beam combination output power of 1062W is obtained.
CLUTTER ELIMINATION IN DEEP EPIPHOTOACOUSTIC IMAGING

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We present a novel method which facilitates clutter cancellation in deep photoacoustic imaging. An epiphotoacoustic setup is preferred for versatile imaging of the human body, with optical irradiation and acoustic probe on the same side. Unfortunately, epiphotoacoustic imaging depth is limited by strong clutter which originates from the strong photoacoustic transients generated at the tissue surface, both directly (direct clutter) and via acoustic scattering (echo clutter). A completely new method now allows substantial clutter cancellation and strongly improved imaging depth in phantom experiments.

1. Introduction
Photoacoustic (PA) imaging of optically absorbing structures inside the body, via the detection of thermoelastic ultrasound after pulsed laser irradiation, is promising for the diagnosis of cancer and vascular disease, and has an especial potential as an additional functional imaging modality to augment conventional ultrasound (US) in a real-time and versatile multimodal device for improved clinical diagnostics [1].

For versatile imaging of the human body, epiphotoacoustic imaging avoids signal loss due to acoustically attenuating tissue by combining all components in one probe for optical irradiation and acoustic detection from the same side of the body. Unfortunately this results in severe clutter which limits imaging depth to typically one centimetre or less. Clutter may emerge from strong PA transients, generated at the site of tissue irradiation close to the probe, which obscure weak signals from deep inside the tissue. Clutter signals may propagate directly to the acoustic probe (direct clutter), or reach the probe via acoustic scattering from echogenic structures (echo clutter) [2, 4].

Versatile deep (several cm) clinical PA imaging thus requires a method for clutter reduction. For this purpose deformation-compensated averaging [3, 4] was shown to improve the signal-to-clutter ratio, and is under continued development. Now we have developed a completely new method which allows full clutter cancellation.

2. Materials and Methods

2.1 Epiphotoacoustic setup
For PA imaging a commercial US scanner was used, the z.one™ (Zonare Medical Systems Inc., USA), with a linear array probe (L10-5, Zonare, -3 dB bandwidth 5-10 MHz). For PA signal generation, a Q-switched Nd:YAG laser (ELEN, Italy) was used at 1064 nm wavelength, delivering 70 mJ per pulse with a 7 ns pulse duration, at 10 Hz repetition frequency.

2.2 Phantoms
Phantoms were built from gelatine for tissue-like acoustic properties, and contained TiO₂ powder for optical scattering and cellulose for echogenicity. For the assessment of the effect of clutter cancellation on contrast and imaging depth, 2-mm-diameter gelatine cylinders were embedded in the phantom, imitating blood vessels. The optical absorption coefficient was tuned to 5 cm⁻¹ using India ink, and no cellulose was added so that they were hypoechoic and could be identified on B-mode US. The effective attenuation coefficient of the bulk gelatine was determined to 1.5 cm⁻¹ based on the depth-dependent amplitude of the PA signal of the absorbing inclusions.

3. Results and Discussion
Fig. 1(a,b) shows the normal echo US image obtained with the z.one™ side-by-side with a photograph of a section through the phantom which was taken after the experiment. Due to the alignment of the imaging plane perpendicular to the cylindrical inclusions, the inclusions are nicely seen as circular regions both in the photograph and in the B-mode US.

Fig. 1c is the conventional PA image obtained at the same location as the echo US. The PA image is also shown in brightness (B) mode like the echo US, i.e. after envelope detection and logarithmic compression. Note that only the middle 19 mm of the 38 mm aperture (the central 64 array elements) was used for PA imaging. Most of the PA image is covered by a diffuse background speckle, which limits the visibility of the absorbing inclusions. Only the uppermost two inclusions can be identified, indicating an imaging depth of 10 mm.

Fig. 1d is the PA image after clutter cancellation, which shows strongly improved contrast and imaging depth, compared to 1c. Inclusions can be seen down to 30 mm, i.e. the imaging depth was three times that of conventional epiphotoacoustic imaging. This improvement confirms what was known from the phantom construction, that the background speckle in Fig. 1c is largely clutter, rather than being related to true PA image signal.
Note that, as is typical for epiphotoacoustic imaging, only the upper and lower edges of the absorbing inclusions can be seen, because the limited aperture and bandwidth of the imaging transducer acts as a directional high-pass filter.

Figure 1: a) Photograph of a section through the phantom at the location of the imaging plane, taken after the experiment. b) B-mode echo ultrasound image of the phantom. c) Conventional epiphotoacoustic image. d) Epiphotoacoustic image after clutter cancellation.

4. Acknowledgement

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References
A combination of the photothermal technique with diffuse reflectance spectroscopy is presented. This combination leads to a new method named photothermal diffuse reflectance (PTDR) and allows combining the high spectral selectivity and strong absorption of the mid-infrared with the large scattering cross-section and high detector sensitivity available at near-infrared wavelengths. The potential of the photothermal diffuse reflectance technique is illustrated by experimental signals obtained from various scattering media like polymers and powders.

1. Introduction

Various photothermal techniques are used for investigating optical absorption and for characterizing thermal properties such as thermal conductivity and thermal diffusivity of materials [1,2]. Among them photothermal reflectance (also called modulated optical reflectance) is an effective non-destructive evaluation technique where the material under investigation is excited with an intensity-modulated laser beam (pump laser) leading to a periodic variation of the local temperature of the sample surface due to the heat produced by the absorbed pump power [3-4]. The temperature change then induces a periodic variation of the sample's refractive index, which can be detected by measuring the modulation in the sample reflectance using a probe beam (probe laser) that is reflected from the sample surface. Photothermal reflectance methods have proven to be especially valuable for investigating highly opaque materials and have been used extensively in several areas of science and technology, particularly for studies of thermal conductivity of thin films [5], thermal conductance of interfaces [6], and thermal diffusivity of solids [7].

Light reaching a scattering medium can be reflected by the surface (specular reflection) or can enter the medium. The light that enters the medium can then be absorbed, transmitted or scattered. Usually a part of the scattered light can return to the surface and escape the scattering medium leading to diffuse reflectance (or remittance). A widely used diffuse reflectance measurement scheme employs a laser to provide a small light input spot on the scattering probe and an optical fiber to collect the light remitted at a given distance (typically some millimeters) from the laser input spot. The main advantage of this scheme is that the whole measurement is conducted from the same side of the sample. Diffuse reflectance is an excellent non-destructive sampling tool for powdered and solid materials. It is also widely utilized for medical diagnostic purposes, such as non-invasive optical spectroscopy of the brain, breast, muscle, and other tissues.

In order to combine the advantages of the photothermal techniques with those of the diffuse reflectance method, we excite a scattering sample with mid-infrared light (pump beam) which, when absorbed by the sample, generates a temperature increase. Simultaneously, the sample is irradiated with a near-infrared light beam, which is only marginally absorbed but strongly scattered by the sample. A strong diffuse reflectance signal modulated by the pump (mid-infrared) beam is thus obtained. Using two excitation beams has many advantages as it combines the high spectral selectivity and absorption cross-section typically observed in the mid-infrared region with the stronger scattering cross-section and higher detector sensitivity available in the near-infrared.

2. Experimental method

The experimental arrangement used for photothermal diffuse reflectance measurements utilizes an external cavity quantum cascade laser (Daylight Solutions, San Diego) tunable between 1025 and 1095 cm⁻¹ and providing more than 60 mW. This laser is used to generate the pulses that heat the sample. A temperature-stabilized and collimated near-infrared diode laser (780 nm, ca. 20 mW) is used as probe beam to illuminate the scattering sample surface near the pump beam. The near-infrared beam is amplitude-modulated at 27 kHz frequency. A part of the scattered light escaping the sample is collected by a plastic optical fiber (step-index PMMA, diam.=1 mm) and fed to a photodiode (New Focus, Model 1801). The photodiode signal is detected by a lock-in amplifier (Stanford Research, SR830) with a 100 ms time constant. A computer controls the triggering signal for the quantum cascade laser (pump) pulse and records the time evolution of the lock-in output.

3. Results and discussion

A typical signal output is presented in Figure 1. The excitation geometry is shown on the right side of Figure 1. Both lasers (mid-infrared (MIR) pump and near-infrared (NIR) probe) are separated by 1.3 mm and the scattered light from the sample, in this case a white turbid polymer sample (PolyOxyMethylene), is collected by the optical fiber located 5 mm apart. The lower line shows the time-dependent signal of the collected scattered near-infrared light without mid-
infrared excitation. A flat baseline is obtained. The upper line presents the output signal using a 500 ms, 52 mW mid-infrared (pump) pulse. This line clearly shows an increase of about 0.2% of the diffusively scattered light after the mid-infrared pump pulse. Comparing the time-evolution of this signal with a finite-element-based numerical simulation of the temperature change at the near-infrared input spot shows that both follow a similar temporal pattern. Further experiments prove that the temporal profile of the photothermal diffuse reflectance signal depends on the distance between the mid- and near-infrared input spot but not on the location of the collecting fiber. This implies that the time evolution of the photothermal diffuse reflectance signal is directly related to the temperature change at the near-infrared input spot. The 0.2% increase of the diffuse reflectance intensity almost corresponds to the expected reflectivity change at the near-infrared input spot due the variation of the sample's refractive index with temperature. Photothermal diffuse reflectance signals for powder sample have also been investigated and will be presented. The wavelength tunability of the quantum cascade laser (pump) will also permit to investigate the spectral dependence of the photothermal diffuse reflectance signal with the pump wavelength.

Figure 1: Temporal evolution of the photothermal diffuse reflectance signal for a polymer sample (PolyOxMethylene, POM) with and without mid-infrared excitation.

4. Conclusion
Using the photothermal diffuse reflectance method, temperature changes due to mid-infrared light absorption are detected through the variation of the diffuse reflectance. The use of two (i.e. a pump and a probe) wavelengths offers a large choice of applications since each wavelength has its own absorption and scattering cross-sections. In the work presented above, this allowed exploiting the benefits of both the mid-infrared high absorption cross-section and the strong scattering cross-section of the near-infrared. Compared to regular photothermal reflectance spectroscopy, the technique presented above doesn't require a flat reflecting surface but can also be successfully implemented on rough surfaces. Photothermal diffuse reflectance is thus a promising spectroscopic method for the studies of scattering, opaque or turbid samples.

References
The use of a Fabry-Perot interferometer (FPI) as line detector in photoacoustic imaging is demonstrated. This work gives a comparison of FPI with a Mach-Zehnder interferometer (MZI) and a piezoelectric line detector. Sensitivity and resolution are shown quantitative and first tomographic images are presented.

1. Motivation

Using optical line detectors for photoacoustic imaging was recently shown by Paltauf et al. [1]. The application of optical interferometers as line detectors has several benefits [2-4]. An interferometer beam propagating in a clear coupling liquid (usually water) is acoustically and optically transparent. Piezo-electric sensors, on the other hand, disturb the acoustic wave and are sensitive to pyro-electric disturbance [5]. Even very small changes in the refractive index caused by ultrasound waves can be detected. The resolution is theoretically limited only by the wavelength of the used laser. Therefore with the right adjustment such a detector promises a highly sensitive, high resolution imaging device for photoacoustics.

2. Experimental setup

The acoustic sensor is a laser beam inside a Fabry-Perot cavity that consists of two concave mirrors. The choice of the radius and the reflectivity of the mirrors is based on simulations. The finesse as a function of the reflectance was calculated for different lengths of the reflector. For the first setup (see Fig. 1) concave mirrors with a radius of 100 mm and a reflectivity of 99.5 % were used and the resonator was built up in a confocal arrangement. To obtain acoustic coupling, the sample and the detection beam must be located in a water tank. The water tank is equipped with windows, which are anti-reflex coated. One concave mirror is mounted onto a piezo-actuator, which is connected to a control unit to stabilize the interferometer. The two mirrors, the first lens and the water tank are fixed relative to each other on a rigid frame to minimize disturbances from vibrations of the surroundings. The estimated finesse in the simulations for this setup is about 36. Fig. 2(a) shows the interferometer output function during a scan of the piezo actuator. From this measurement a finesse of 27 can be derived.

3. Experiments

Figure 2(b) shows the simulated (black line) and measured (red line) signal of a small disk-like source with a diameter of 600 µm as it is received with the line detector. In the experiment, the phantom consisted of gelatin dyed with black ink. The phantom was irradiated with pulses having a wavelength 532 nm and guided to the phantom with a waveguide. The tip of the fiber with a diameter of 600 µm was imaged onto the surface of the gelatin-ink-mixture. The simulated and measured data are in good agreement.
4. Outlook

The mirror separation and curvature have to be optimized to decrease the beam diameter in the resonator since this diameter limits the resolution of the acoustic sensor. Also the sensitivity is to be measured quantitatively for comparison of the Fabry-Perot-interferometer with the Mach-Zehnder-interferometer and with piezoelectric line detectors.

References

OPTOACOUSTICS AND FTIR SPECTROSCOPY
IN THE STUDIES OF OLD PAPER SAMPLES

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The possibility of the very fast paper degradation (yellowing) due to oxidation of the cellulose fibers and formation of yellowish-brown spots (foxings) is known. The comparison of porosities of old paper samples in foxings and foxing-free fragments is completed. Optoacoustic method to determine the porosity of four different old paper samples inside and outside foxings are presented. The porosities of paper samples are calculated using the measured velocities and employing the theory of two-phase mixture. FTIR spectroscopy is employed to diagnose the structural changes in all the samples.

Modern technologies including laser ones and physical methods are widely used in various fields of natural sciences as well as in humane sciences such as arts. Objects of cultural heritage can be strongly exposed to the surrounding medium. This accounts for the topicality of the development of the methods for diagnostics, restoration, and conservation of these objects.

In this work, we study the old paper materials. Specific interest in such a study is related to the possibility of the very fast degradation of paper due to oxidation of the cellulose fibers (yellowing) and formation of yellowish-brown spots (foxings) [1].

A commonly accepted interpretation of the nature of foxings is missing, but two main concepts are discussed. The first one considers foxings as a result of ultrafast oxidation catalyzed by iron impurities on the surface of paper. According to the second idea, foxings result from microorganism activity. The existing experimental data can be used to prove both hypotheses. Presumably, both concepts are correct since paper is a highly inhomogeneous object and varies processes are involved in paper aging. Thus, any data characterizing the modification of paper with time are significant.

The main purpose of this work is the comparison of paper porosities in foxings and foxing-free fragments. We use optoacoustic (OA) method [2] to determine the porosity of four different paper samples inside and outside foxings. The samples have different compositions and structures. Sample S1 is a page from the book "Methods in Russian grammar" printed in Russia in 1926. Samples S2 and S3 are the paper sheets from the documents printed in the 1850s and 1950s, respectively. Sample S4 is a pure cotton paper produced in 1990.

For the excitation of the probing acoustic pulse we use the radiation of the Nd³⁺:YAG laser with a wavelength of 1.06 µm, a pulse duration of 10-12 ns, the pulse energy ranging from 10 to 15 mJ, and a repetition rate of 2 Hz. The laser pulses are absorbed by the SZS-22 color-glass filter, which serves as the OA source. The thermo-optical effect provides the excitation of the broadband ultrasonic signals. The paper samples immersed in two liquids (ethanol and transformer oil) are pressed between the OA source and the broadband piezoelectric receiver based on LiNbO₃ crystal (the working frequency band is 1-100 MHz). We measure the time delay of the ultrasonic pulse having passed through the sample and determine the velocity of the longitudinal acoustic waves. For the measurement of the electric signal, we employ a Tektronix TDS-1012 digital oscilloscope with an analog frequency band of 100 MHz. Averaging over 128 samples is performed.

We calculate the porosity of paper samples using the measured velocities and employing the theory of two-phase mixture [2]. Within experimental error the porosity of paper in foxings is no less than the porosity of unfoxed paper. The difference of the corresponding porosities for samples S1 and S2 is 12-15 %. This result indicates significant modification of paper in foxings.

FTIR spectra of samples (upper curves) S2 and (lower curves) S3 measured at (dashed lines) foxing spots and (solid lines) unfoxed regions.
However, FTIR spectra show the structural changes in all the samples under study. Vibrational spectra are measured using a Nicolet 6700 FTIR spectrometer interfaced with a Smart Orbit ATR unit. A Parker Balston Lab Gas Generator is used for purging with dry air. The spectral range and resolution are 400-4000 cm\(^{-1}\) and 2 cm\(^{-1}\), respectively. We analyze the spectral interval 1500-1800 cm\(^{-1}\), which corresponds to the vibrations of ketonic and carboxylic groups and is sensitive to the oxidation of paper. The figure shows that the intensities of the vibrational bands in the spectra of foxings are significantly greater than the intensities of the bands corresponding to the foxing-free regions.


The optoacoustic method has been shown to be an accurate technique for the measurement of the properties of submicron metal coatings deposited on a dielectric substrate, i.e. mirrors. The method has been previously theoretically described in terms of a linear model of optoacoustic (OA) transformation in a system substrate/coating/liquid. The goal of the present work was to determine the limits at which the linear model is still applicable and study the possibility of using the nonlinear OA transformation as an additional tool for diagnostics of coating properties.

In the linear regime of OA transformation all physical parameters of the three-layered system are assumed to be constants which are not dependent on the temperature. The primary nonlinear component of the OA transformation in the system under study can be described by the nonlinearity of the thermal expansion coefficient of the liquid, so called thermal nonlinearity of the liquid [1]. The finite difference method was used for the numerical solution of nonuniform wave equations.

Chrome metal coatings deposited on the quartz substrate were used in experiments. The thickness of the coatings was determined earlier by the method proposed in [2, 3] under the assumption that the thermal diffusivity of coatings is known. The coatings were in contact with water or ethanol. The forward mode [3] of the OA signal detection (laser pulse is incident from the side of the substrate, and the detection of excited OA signals is performed in the liquid) was used.

It has been demonstrated that in the case of ethanol, the OA signal shape does not change until laser fluence reaches a threshold depending on the coating thickness. Beyond the threshold the OA signal amplitude grew dramatically. Such a strong and sharp growth of the OA transformation efficiency cannot be explained by the thermal nonlinearity alone and it is more likely that within the laser pulse duration a thin layer of ethanol may be involved in phase transition processes. The ethanol vapor has a much higher thermal expansion coefficient compared to the liquid phase that produces the sudden increase in the efficiency of the OA transformation.

Contrary to the ethanol, in case of water the growth in the OA excitation efficiency occurs gradually with the increase of the laser fluence. Numerically calculated spectral transfer function demonstrate a good agreement with measured ones thereby proving the strong influence of thermal nonlinearity effects in the system under study.

Thus, the applicability limits of the OA method for the metal coating evaluation have been quantitatively described. It has been shown that the use of deionized water is not optimal in that method and can lead to essential mistakes in the coating properties to be determined due to the nonlinear effects. On the other hand, nonlinear effects described above can be used as an additional tool in diagnostics of coating properties and particularly to determine coating thermal diffusivity when it is a priory unknown.

References

EXPLOSIVE BOILING OF TRANSPARENT LIQUIDS ON ABSORBING TARGETS HEATED BY SHORT LASER PULSES

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Abstract

Explosive boiling induced by sub-nanosecond laser pulses is theoretically analyzed in the case of transparent liquids on metal targets. In this case the variation of boiling start times can probably be reduced to laser pulse duration so that photoacoustic pressure signal could become less distorted due to inhomogeneous distribution of laser intensity through the irradiation spot. The results are compared with experimental investigations of photoacoustic signals induced in metal target under transparent liquid layer irradiated by laser pulses of about 100 ps duration and wavelength 532 nm.

Explosive boiling including the case of transparent liquids on absorbing targets heated by laser pulses was studied for many years. Nevertheless there are some unresolved important questions in this problem, in particularly concerning with time dynamics of the process and its peculiarities in near-critical region. Explosive boiling can only occur when the pressure in the heated zone $P$ is lower than critical pressure $P_{cr}$ and this fact can be used to experimentally determine critical pressure value. During the process of laser ablation in sub-critical region explosive boiling can manifest itself as multiple pressure peaks in photoacoustic signal from the irradiated zone [1].

Earlier, with the exception of work [2], no such peculiarities in pressure behavior were observed for nanosecond laser ablation. On the other hand the pressure increase due to explosive boiling was observed e.g. in [3] as increase of shock-wave velocity in ambient atmosphere near the irradiated target. Explosive boiling also took place in the experiment [4] where the process of ejection of thin transparent liquid film from the laser heated target was observed. However in this case the pressure behavior was also not directly registered.

It is clear that the registered pressure rise time in explosive boiling can significantly exceed the real rise time of the process if the radiation intensity is not constant over the radiation spot due to variation of explosive boiling start time in different points. It is possible to reduce this effect by diminishing of space variation of radiation intensity or using sufficiently short laser pulses. In the later case the variation of boiling start times reduces to laser pulse duration provided it is not too short compared with the nucleation time. It should be mentioned further that laser pulse duration determines the photoacoustic pressure value in the boundary region between liquid and target. If this pressure significantly exceeds the saturation pressure of liquid at achieved temperature then no explosive boiling occurs during laser pulse action. In the present work theoretical analysis of various aspects of such regimes are considered.

The theoretical conclusions are compared with experimental results obtained for the case of transparent liquid on metal targets heated by laser radiation with wavelength 532 nm and pulse duration ~0.1 ns. Pressure signals from irradiated zone were measured with piezoelectric transducer (LiNbO3) working in current source regime.

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References

NEAR-IR LASER-BASED SYSTEM FOR $^{13}$CO$_2$/$^{12}$CO$_2$ RATIO ANALYSIS IN BREATH

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A laser based analyzer of the relative content of CO$_2$ isotope modifications in exhaled air is presented. The system operates at 2.05 micron spectral region and is intended for isotope analysis in breath tests based on application of chemicals enriched with stable carbon isotope $^{13}$C. The two-channel optical scheme of the system and the special digital system for its control including the original software were developed for spectral data acquisition and development. An algorithm of spectral data processing aimed at determining the difference in the isotope composition of gas mixtures is proposed. A few spectral regions near 4880 cm$^{-1}$ are determined to be optimal for analysis of relative content of $^{12}$CO$_2$ and $^{13}$CO$_2$ in the exhaled air. Due to applied optical and electronic schematics high accuracy and sensitivity of the isotope analysis was achieved with the analyzer when operating at room temperatures. Achieved sensitivity of the comparative analysis of the isotope content of CO$_2$ in exhaled air samples is estimated to be nearly 0.01%.

The possibility of using the laser-based methods for high-sensitivity analysis of CO$_2$ isotope composition has been repeatedly discussed. In particular, laboratory systems based on tunable diode lasers (TDL) aimed at measuring the relative content of $^{12}$CO$_2$ and $^{13}$CO$_2$ were reported [1-5]. The urgency of these products is due to their use in medical diagnostics based on the isotope testing of exhaled air [6]. It is essential that these tests do not require measurement of the absolute concentrations of $^{12}$CO$_2$ and $^{13}$CO$_2$. It is sufficient to determine the change in the isotope content of the exhalate air, caused by administering the $^{13}$C-labelled preparations. It is always supposed that there are two or more samples of the gas mixture whose isotope composition may slightly differ. The analysis of publications [1,4,5] shows that this specific feature is not taken into account by the researchers even when double-beam or differential optical schemes are used, although this could provide the required analytic characteristics using more simple and reliable methods.

The use of TDLs for the analysis of isotope composition of CO$_2$ in the exhaled air is quite adequate to the complexity of the considered problem. The wide spectral range covered by lasers of this type allows the choice of the spectral region most suitable for the analysis. The tuning characteristics of TDLs allow simultaneous recording of both $^{12}$CO$_2$ and $^{13}$CO$_2$ absorption lines. The DLS methods can provide recording of relative changes in the optical density in the absorption lines at the level of $10^{-6}$ – $10^{-7}$ [7-9] and solving the problems of optical diagnostics with the use of weak absorption bands. Finally, the all-electronic control of the TDL radiation parameters allows application of novel digital methods for recording and processing of the spectral data and, thus, significant reduction of the noise level.

The spectrophotometer aimed at high sensitivity (with the accuracy of ~0.01 %) quantitative analysis of differences in the isotope composition of CO$_2$ in exhaled air samples and based on the use of a TDL operating in the near-IR range (2.05 µm) is reported. Original schemes and constructions of the laser analytic unit, electronics and software, as well as algorithms for spectral data processing, are used in the presented system [10]. The system can serve as a prototype analyzer for clinical applications, associated with isotopic diagnostics of digestive apparatus diseases.

For the isotope analysis using a TDL operating at room temperature, the spectral region near 2.05 µm was chosen. In this region the R-branch of the 20013 – 00001 band of $^{12}$CO$_2$ overlaps with the P-branch of the 20012 – 00001 band of $^{13}$CO$_2$ [11], which makes it possible to choose a pair of closely spaced lines of $^{13}$CO$_2$ and $^{13}$CO$_2$ convenient for the analysis. For the gas mixture corresponding to the composition of the exhaled air, the absorption coefficient in the peaks of the most intense CO$_2$ lines of this band amounts to $3 \cdot 10^{-5}$ cm$^{-1}$. With such an absorption coefficient and sensitivity to absorption at the level of $3 \cdot 10^{-3}$, achievable using TDLs [7,8], the required concentration sensitivity can be implemented for the optical path length equal to ~100 cm. The additional technical requirement is that the volume of the gas sample should not exceed 100 mL, which is determined by the volume of the container for collecting the samples of exhale air.

The mentioned specific features of the problem under solution were taken into account in the design of the spectrophotometer based on the distributed-feedback TDL operating at room temperature near the wavelength 2.05 µm. The precise tuning of the optical frequency of the laser radiation was performed by varying the laser temperature in the range from –10 to +50°C by a thermoelectric cooler. The repetitively pulsed regime of the TDL pumping was used to provide the frequency scanning. The pulse repetition rate was 200 – 300 Hz, and the pulse duration was 3 – 4 ms. The laser was pumped using electric current pulses with a linearly increasing amplitude, which allowed linearization of the frequency tuning rate during the pulse. In this regime the tuning rate of the laser radiation frequency was ~2 cm$^{-1}$ ms$^{-1}$, and the frequency changed by 5 – 8 cm$^{-1}$ during a single pulse. The laser radiation power amounted to ~0.5 mW. The TDL temperature was stabilised with the accuracy up to ~10$^{-3}$ grad. Together with the high reproducibility of the
current pump parameters (the duration, the pulse period, and the amplitude), this provided the required reproducibility of the frequency tuning, the radiation amplitude and the transmission spectra recorded.

The specific features of the spectrophotometer scheme provide sufficient absorption in the analytic lines, simultaneous analysis of the reference (basal) and the analysed (control) gas mixtures, close laser radiation intensities and equality of temperatures in the two optical channels. The optical beam, outgoing from the laser crystal, was collimated into a parallel one by an aspherical lens with the focal length ~8 mm. The beam width was limited using an aperture with the diameter ~5 mm. Using a beamsplitter, the beam was split into two beams with nearly equal intensities, each passed through one of practically identical multipass cells 200 mm long. The multipass regime was implemented using two plane mirrors. The number of the ray passes in each cell was 14, so that the total optical path length in each cell was ~280 cm. After leaving the cells, laser radiation was focused onto the InGaAs photodetectors cooled to ~50°C. The cells with inner volume ~50 cm³ each were made of duralumin, and their construction, providing good thermal contact with the base of the optical unit, ensured practically equal temperatures of the gas samples in both cells. Each cell was equipped with branch pipes to provide the gas circulation. Operation of the spectrophotometer is based on using the original software – hardware complex that consists of three digital units providing the TDL temperature stabilisation, the TDL pumping, and the control of the transmission spectra recording. The scheme of the latter unit is based on the use of programmable logical matrices (Altera) and fast high-bit number ADCs (Texas Instruments). The sampling rate of the laser signal is 5 MHz, and the discreteness is 16 bit. This unit provides simultaneous and independent recording of laser spectra in two optical channels. The high sampling rate of the signal and the data exchange between the recording system and the controlling computer, corresponding to the protocol USB 2.0, allows recording all laser pulses in both channels simultaneously. Using the software of the controlling PC, operating under the WindowsXP/Vista OS, the following features are implemented and displayed: the system control terminal, the process of the complex control, the introduction of the system parameters, the choice of algorithms for spectral data processing, the real-time visualisation of the recorded spectra and the visualisation of the results of the spectral data processing.

To provide the required accuracy of the isotope composition analysis of the exhale air samples, a special algorithm that allows detection of very small variations in the absorption spectrum of the analysed gas mixture with respect to the spectrum of the reference mixture was proposed and implemented. Due to this algorithm, the obtained results become insensitive to the influence of the general CO₂ concentration changes, to the variations in the environment temperature and to the parameters of laser radiation, which may cause random or systematic errors.

Thus, we have developed the laser spectrophotometer aimed at high-accuracy comparative analysis of ¹²CO₂ and ¹³CO₂ isotope content in the exhale air samples and based on the use of tunable diode lasers in the near-IR region (2.05 µm). The spectrophotometer uses the two-channel optical scheme, small volume multipass cells and special all-digital control system. The analysis has been implemented using a simple algorithm for spectral data processing, aimed at determining the difference in the isotope composition of gas mixtures. Several spectral regions (near 4878 and 4882 cm⁻¹) are proposed as optimal for isotope analysis of CO₂ in the exhale air. The use of the proposed spectrophotometer scheme allows minimisation of the effects of interference in optical elements, absorption in open atmosphere, slow drift of the envelope function of the laser pulse, and offset of spectral channels. This is achieved at the expense of providing high reproducibility of the spectral characteristics of laser radiation, as well as simultaneous and independent high-speed recording of spectra in the reference and analytic channels. The use of two thermally coupled optical channels allows neglecting the temperature difference between the analytic and reference gas mixtures. The influence of random noise on the result of the isotope analysis using the proposed algorithm is estimated. It is shown that if the sensitivity with respect to resonance absorption is ~10⁻⁷ and the optical density in the absorption peaks of the analytic lines is ~10⁻² the sensitivity of the isotope analysis can be ~ 0.1 %.

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References
Ultrafast thin disk lasers (TDLs), passively modelocked with semiconductor saturable absorber mirrors (SESAMs), currently achieve higher pulse energies and average powers than any other oscillator technology. They are therefore excellent candidates for driving extreme nonlinear optics experiments at megahertz repetition rates in systems with the footprint of a low power oscillator. The extremely high intracavity intensity offers a new avenue to boost the average photon flux in high harmonic generation (HHG) and therefore generate a table-top source of vacuum ultraviolet (VUV) and extreme ultraviolet (XUV) radiation. However, previously, the pulse duration from TDLs was too long for efficient HHG. Furthermore, the potential of these sources as stabilized frequency combs was not demonstrated. Here, we review the first ultrafast TDL generating pulses in the sub-100 fs regime and the first carrier envelope offset (CEO) frequency measurement of a TDL. These results open promising possibilities for intralaser extreme nonlinear optics such as megahertz HHG and VUV/XUV spectroscopy using unamplified high-power oscillators with excellent noise properties.

1. Introduction

SESAM modelocked thin disk lasers (TDLs) generate pulse energies >40 µJ and average powers > 140 W in femtosecond pulses [1, 2] making them excellent candidates for driving extreme nonlinear optics experiments at megahertz repetition rates, in systems with the footprint of a low power oscillator [3].

2. Experimental results

For the sub-100 fs TDL (Fig 2a) we used a 200-µm thick Yb:LuScO_3 disk mounted on a 1.4-mm thick diamond, water cooled directly through the back. We used a Volume Bragg Grating stabilized pump with a narrow linewidth < 0.5 nm at 976 nm. The pump module was arranged for 24 passes through the disk and the pump spot diameter was 1.9 mm. In order to achieve soliton modelocking, we introduced 5 GTI-type mirrors that introduced 2800 fs² of negative dispersion per roundtrip and two YAG plates (5- and 7-mm thick) to introduce self-phase modulation (SPM) to balance the introduced dispersion. We used a 2.6% output coupler (OC) and a SESAM with a saturation fluence $F_{\text{sat}} = 36 \mu J/cm^2$, modulation depth $\Delta R = 3.3\%$, nonsaturable losses $\Delta R_{\text{ns}} = 0.7\%$ and a fast recovery time of $\tau_{1/e} = 1.9\ ps$. Stable modelocking was obtained with up to 5.1 W of average power at a pulse duration of 96 fs, with an optical-to-optical efficiency of 11% (Figure 2a). The laser operated at a repetition rate of 77.5 MHz. The time-bandwidth product (TBP) of the pulses was 0.33 (ideal for sech² pulses 0.315). These are, to our knowledge, the shortest pulses ever obtained with a modelocked TDL, reaching for the first time the sub-100 fs regime.

The experiment on CEO frequency detection was performed on a second laser setup (Fig. 2b), based on a different gain material (Yb:Lu_2O_3). The pump arrangement was the same as in the previous laser setup. The disk was 150-µm thick, 3%-doped, was mounted on a 1.4-mm thick diamond and soldered on a back-cooled copper heatsink. In order to achieve soliton modelocking we introduced 2 GTI-type mirrors (-2200 fs² dispersion per roundtrip) and a 1.5-mm thick YAG plate to introduce self phase modulation (SPM). We used a 4% OC and a SESAM with $F_{\text{sat}} = 35 \mu J/cm^2$, $\Delta R = 3.4\%$, $\Delta R_{\text{ns}} = 0.8\%$ and $\tau_{1/e} = 1.9\ ps$. We obtained pulses as short as 142 fs at an average power of 7 W and an...
optical-to-optical efficiency of 15%. The repetition rate was 64 MHz. The pulses had a TBP of 0.34. 65 mW of the laser output were enough to generate a stable octave-spanning supercontinuum (SC) in a 1-m long, highly nonlinear photonic crystal fiber (PCF) (Fig2b middle). The SC was launched into an f-to-2f interferometer [6] for CEO beat detection. The signal-to-noise ratio (SNR) of the CEO beats was > 25 dB in a resolution bandwidth (RBW) of 3 kHz (Fig 2b right) and > 30 dB in a RBW of 1 kHz. The CEO beat frequency was tunable by the pump current, with a slope of ≈ 33 kHz/mA. This mechanism will be used for electronic stabilization of the CEO frequency to an external reference. It is worth emphasizing that CEO detection was possible despite the strongly multimode pumping scheme of TDLs, usually associated with a high noise level.

3. Conclusion and Outlook
We demonstrate 5.1 W, sub-100 fs from a TDL based on the broadband sesquioxide material Yb:LuScO3. These are the shortest pulses ever obtained with a modelocked TDL, reaching for the first time the sub-100 fs regime. In addition, we obtained pulses as short as 142 fs using the record holding material Yb:Lu2O3—which only has 12 nm of gain bandwidth [1]. Using larger disks, larger spot sizes and by designing SESAMs with reduced two photon absorption and higher damage thresholds [8], we expect kW intracavity powers with sub-100 fs pulses in the near future. The achieved progress in terms of pulse duration enabled us to measure the first CEO beat of a TDL using a standard f-to-2f interferometer [6, 7] without any external amplification or pulse compression. The detected CEO beats had a sufficiently large SNR to stabilize the laser system with the pump current. In the near future, frequency combs in the 100-W regime from unamplified laser oscillators appear feasible. Although the output powers obtained in these proof-of-principle experiments are moderate, we demonstrate an intracavity power >200 W in sub-100 fs pulses, reaching an interesting starting point for intralaser nonlinear optics experiments. These results prove the suitability of modelocked thin disk lasers for future intralaser nonlinear optics experiments.

Acknowledgments
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We report on thulium-doped all-fiber lasers based on the nonlinear amplifying loop mirror and mode-locked with both a semiconductor saturable absorber and single-walled carbon nanotubes. An intracavity and external dispersion management was realized inserting a section of a passive germanium-silicate fiber. Lasers generate as short as 230-fs and 450-fs pulses near $1.9 \mu m$ wavelengths respectively. The maximum average output power reached 106 mW, corresponding to a 3.7 kW peak power and almost 2 nJ pulse energy.

1. Introduction

Thulium-doped mode-locked fiber lasers have attracted considerable attention due to a very wide gain spectrum, extending from 1.8 to 2.1 $\mu m$ and a high lasing efficiency, which are useful for spectroscopy, LIDARs, medicine, and semiconductor micromachining.

Earlier different schemes incorporating SESAMs and SWCNT saturable absorbers have been reported for thulium-doped mode-locked dispersion-managed fiber lasers [1-4]. Most of them were built in linear, ring or figure-of-eight cavity geometries. Here we present both SESAM and SWCNT mode-locked thulium-doped fiber lasers in a sigma-cavity layout based on the nonlinear amplifying loop mirror (NALM) as an additional saturable absorber. Due to the intensity dependent reflectivity the NALM incorporation into laser cavity provides efficient self-switching, pedestal suppression and pulse shaping. NALM benefits from breaking symmetry in the loop with the aid of unequal splitting ratio of the NALM forming fiber coupler, the gain implementation, and appropriate linear phase delay through polarization control [5,6].

2. Experimental setup

A 1.5-m-long fiber loop mirror is formed using a 20:80 fiber coupler. Here a 0.7 m-long section of a step-index ($\Delta n = 0.012$) thulium-doped aluminum-silica glass fiber is positioned close to the NALM forming coupler inside the loop. The active fiber dispersion was measured to be $\beta_2 = -76 \text{ ps}^2/\text{km}$ at the wavelength of laser generation. Pump radiation of 1 W maximum power from a CW erbium-ytterbium co-doped fiber laser is coupled into the laser cavity through a 1.56/1.9 $\mu m$ wavelength division multiplexer (WDM) in a clockwise direction of the NALM.

A short section of low-loss normal dispersion ($\beta_2 = +280 \text{ ps}^2/\text{km}$) highly nonlinear ($\gamma = 15 \text{ W}^{-1} \cdot \text{km}^{-1}$) germanium-silica (GeO$_2$/SiO$_2$) fiber is spliced into the fiber loop to control the overall net cavity dispersion. A squeezing hand-made polarization controller (PC) placed inside the loop provides an efficient lasing wavelength tuning as well as helps to appropriate adjustment of the NALM operation regime.

2.1 SESAM mode-locked thulium-doped fiber laser

The experimental schematic of the SESAM mode-locked laser containing aforementioned NALM is presented in Fig. 1.

![Figure 1: Layout of SESAM mode-locked thulium-doped fiber laser. Inserts: pulse trains](image)

A SESAM [10], initiating the mode-locking generation, is attached face-to-face to the 80% coupler output. An additional commercially available polarization controller is positioned outside the NALM to ensure stable single-pulse mode-locking and to improve pulse characteristics.

In order to compensate an excess pulse chirp, a short section of the same GeO$_2$/SiO$_2$ fiber was implemented outside laser cavity, creating the appropriate external dispersion delay line.
The shortest pulse duration of slightly less than 230 fs with a spectrum FWHM of 26.4 nm was achieved in the case of intracavity and external GVD values of \(-0.054\) ps\(^2\) and \(-0.031\) ps\(^2\) respectively and pump power level of 310 mW. The output spectrum and autocorrelation trace of pulse intensity are presented in Fig. 3 (red plots).

By a pump power increase from 310 mW up to 1 W the laser has been still operating steadily without perturbations in a single-pulse regime generating \(~300\) fs pulses with 3-dB spectral bandwidth of \(~23.5\) nm. The maximum average output power reached 106 mW, corresponding to the maximum pulse energy of \(~2\) nJ and the peak power of 3.7 kW.

### 2.2 SWCNT mode-locked thulium-doped fiber laser

The laser setup is presented in Fig. 2. Laser cavity is formed by linear and the aforementioned nonlinear fiber loop mirrors. The linear mirror (FLM) provided reflectivity of 88% at 1.9 \(\mu\)m. SWCNT film is fixed between two angle-polished ferrules of optical connectors and positioned at the 80% NALM forming coupler output.

The SWCNTs were synthesized by the arc discharge method as they providing an optical absorption band shifted to IR-wavelength range comparing to the absorption bands of nanotubes synthesized using other methods. Manufacturing and characteristics of stable suspensions of individual SWCNTs in 1 wt% aqueous solution of carboxymethylcellulose (CMC) is described in details in [7]. The most stable mode-locking regime occurs by using two serial films simultaneously in one saturable absorber module providing the total transmission value of 57.6% at 1.9 \(\mu\)m.

The external dispersion was controlled as in the previous experiments and amounted to \(~-0.031\) ps\(^2\).

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**Figure 2:** Schematic sketch of thulium-doped SWCNT mode-locked fiber laser. Insert: pulse trains, CMC films transmission spectrum

The shortest pulse duration of slightly less than 450 fs was obtained at the intracavity dispersion value of \(-0.093\) ps\(^2\). Corresponding spectrum bandwidth reached in this case 15.8 nm. The output spectrum and autocorrelation trace of pulse intensity are presented in Fig. 3 (blue plots).

**Figure 3:** Output pulse characteristics: a) autocorrelation traces; b) spectra

In conclusion we have demonstrated for the first time mode-locked thulium-doped fiber lasers based on NALM generating both a 230-fs pulses with 106 mW maximum average power through the SESAM implementing or a 450-fs pulses with 6.3 mW maximum average power using SWCNT saturable absorber. To the best of our knowledge, we have observed the shortest pulse durations ever generated by SESAM and SWCNT mode-locked thulium-doped fiber lasers.

**References**


Stable frequency combs from femtosecond lasers have been a major breakthrough in optical science and metrology. Typical frequency combs are either based on complex green-pumped Ti:sapphire lasers or amplified fiber laser systems. We have demonstrated the first gigahertz frequency comb based on a more compact diode-pumped solid-state laser. A Yb:KGW (ytterbium-doped potassium gadolinium tungstate) crystal pumped by a high brightness distributed Bragg reflector (DBR) tapered diode laser and a semiconductor saturable absorber mirror (SESAM) provide stable fundamental passive modelocking. This compact diode-pumped solid-state laser reaches an average output power of 2.2 W with an optical-to-optical efficiency of 38% at 1 GHz with a pulse duration of 290 fs at a center wavelength of 1041 nm. Also an even higher repetition rate of 4.8 GHz has been demonstrated at an average output power of 1.9 W, an optical-to-optical efficiency of 36% and a pulse duration of 396 fs at 1043 nm. Femtosecond pulses at Watt level power makes these lasers a promising source for multi-GHz self-referenced frequency combs. First carrier envelope offset (CEO) beat signals have been measured and we will discuss the requirements for stable frequency comb generation using such sources.

1. Introduction

Frequency combs from modelocked lasers serve as a phase-stable link between optical and microwave frequencies. Therefore a frequency comb works like a 'gear wheel' coherently converting an unknown optical frequency of several hundred terahertz into a microwave frequency in the megahertz regime, which can be easily measured. This technology brought a tremendous progress in various fields of science, for instance spectroscopy, precision metrology or optical clocks. Usually self-referenced combs are based on Ti:sapphire lasers or fiber lasers. Ti:sapphire oscillators offer extremely short pulses and exhibit low noise levels, but they rely on complex Kerr lens mode locking (KLM) and demand multi-watt green pump lasers. More convenient and robust systems rely on diode-pumped fiber lasers. However, these lasers suffer from a higher quantum noise and limited repetition rate. Ultrafast diode-pumped solid-state lasers (DPSSLs) are excellent compact sources for frequency combs. They combine the favorable properties of cost-efficient diode-pumping and an intrinsic low quantum noise level. Furthermore, they can achieve watt-level average powers without any amplification, even in combination with high repetition rates, aiming at applications in frequency metrology and nonlinear spectrometry.

2. Stabilizing a frequency comb

Optical spectra of modelocked lasers consist of individual, equidistantly spaced frequencies. Therefore, they are also referred to as frequency combs. Any frequency comb from a modelocked laser has two degrees of freedom; the comb spacing (i.e. the pulse repetition frequency) and the comb offset (i.e. the carrier envelope offset (CEO) frequency). For stabilization of the comb both frequencies have to be determined and locked. Detecting the repetition rate is straightforward and has been established in the 1980s. However, measuring the CEO frequency is more challenging, especially at high repetition rates. The standard f-to-2f interferometer scheme for CEO detection [1] is based on a coherent octave-spanning spectrum (Fig 1).

For generating an octave-spanning spectrum, laser pulses are launched into a highly nonlinear photonic crystal fiber (PCF). The stabilization of the frequency comb requires a highly coherent spectrum. This will be obtained if higher order dispersion and Raman scattering induce the broadening but modulation instabilities and noise amplification are kept low. From realistic numerical simulations solving the generalized nonlinear Schrödinger equation a simple theoretical guideline emerges [2]: A coherent supercontinuum is generated if input pulse soliton order N is below 10,
meaning in particular:

\[
N = \left[ \frac{L_{D}}{L_{NL}} \right] = \left[ 0.283 \cdot \frac{\tau_{p} \cdot P_{av} \cdot \gamma}{f_{rep}} \left| \beta \right| \right] < 10
\]

This guideline sets an upper limit for the pulse duration at a given power level using an appropriate PCF.

3. Compact frequency comb from a gigahertz DPSSL

Frequency combs at higher repetition rates provide increased power per mode and simpler access to individual optical lines. Technologies e.g. ultrafast data transmission, nonlinear spectroscopy or calibration of spectrometers greatly benefit from reliable high repetition rate frequency combs. We investigated the feasibility for high repetition rate frequency comb generation from DPSSLs. We report on the first CEO beat detection of a DPSSL with a gigahertz repetition rate (Fig. 2).

![Fig. 2: 1-GHz Yb:KGW oscillator with pump diode and pump optics (L1, L2, L3), output coupler (M1), curved dispersive mirror (M2), curved mirror M3 and SESAM.](image)

Stable, fundamental cw modelocked operation was achieved with a SESAM. The soliton-modelocked Yb:KGW laser was pumped by a high brightness distributed Bragg reflector (DBR) tapered diode laser [3]. It delivered 2.2-W average power in 290-fs pulses at the repetition rate of 1 GHz. This corresponds to the highest pulse energy ever obtained from a gigahertz DPSSL [4]. We used this laser with and without additional pulse compression to adjust the pulse duration and explore the regime for stable CEO detection and self-referenceable gigahertz frequency comb generation. Launching these pulses directly into a highly nonlinear photonic crystal fiber, corresponding to a soliton order N=13, we generated an octave-spanning spectrum but without any measurable CEO signal. By reducing the pulse duration with a passive prism-compressor to 100 fs at 1.1-W average power a soliton order of N=5 was obtained. The shorter pulses generated a similar optical spectrum, but with significantly better coherence enabling a clear CEO beat signal. These experimental give a first experimental confirmation of the theoretical guideline for coherent supercontinuum generation, as written in equation (1).

4. Multi-GHz femtosecond DPSSLs

Scaling the repetition rate of femtosecond DPSSLs into the multi-GHz regime provides even more compact and reliable high repetition rate frequency combs and paves the way towards frequency combs from optically-pumped semiconductor lasers. Using a similar setup as shown in Fig. 2 we built a diode-pumped Yb:KGW laser emitting at a wavelength of 1043 nm with a pulse duration of 396 fs at repetition rate of 4.8 GHz, which is the highest repetition rate from a femtosecond DPSSL ever reported so far [5]. The average output power of this compact diode-pumped solid-state laser is 1.9 W corresponding to a peak power of 0.9 kW and the optical-to-optical efficiency is 36%. This laser operates in the fundamental modelocking regime in contrast to the harmonic modelocking, which suffers from intrinsically higher noise.

5. Conclusion

We presented a gigahertz DPSSL with record high pulse energy enabling stable frequency comb generation and a femtosecond DPSSL with the highest repetition rate reported so far. The combination of a high repetition rate, femtosecond pulses and a high power level makes the presented laser systems a promising source for multi-GHz self-referenced frequency combs. Due to the fact that no Q-switched modelocking was observed at any pump power even higher repetition rates in fundamental, cw modelocked operation seem feasible. Following a theoretical guideline stable frequency comb generation higher repetition rates require shorter pulse durations, which could be achieved by optimizing the cavity dispersion and employing faster SESAMs.

References

We spectrally broaden 860 fs pulses from a 7.3 W, 3.91 MHz thin disk laser in a 2.8 m long Xe-filled HC-PCF. After compression, we achieve 4.2 W in sub 50 fs pulses at a peak power of 10 MW.

1. Introduction and Motivation

Modelocked Thin Disk Lasers (TDL) currently achieve higher average powers and energies than any other oscillator technology [1, 2]. However, their peak power is limited by the relatively long pulses (>700 fs) achieved at record high power levels. Efficient pulse compression of such sources, resulting in increased peak power levels, will result in tabletop sources ideally suited for fundamental science and technology.

Temporal compression via SPM-induced spectral broadening in fibers is particularly attractive due to the large achievable compression factors and high efficiencies. Previously, 760-fs pulses from a thin disk oscillator were compressed to 24 fs at 32 W average power and 50% overall efficiency using a large-mode area (LMA) silica microstructured fiber [3, 4]. However, pulses with peak power levels above 4 MW cannot be directly compressed in standard fused-silica solid core fibers because self-focusing would occur. Therefore, other methods are needed for temporal compression of state-of-the-art TDLs delivering 10s of µJ with MW peak powers. The damage limitations of solid core fibers can be overcome by spectral broadening inside a gas-filled Hollow-Core Photonic Crystal Fiber (HC-PCF). This combines the advantage of guiding the light in a fiber with the possibility to use gases as nonlinear medium. Kagome-type HC-PCFs have significantly lower field overlap with the surrounding silica structure than other HC-PCFs [5], making them ideally suited for high peak power levels. Furthermore, very low dispersion and an ultrabroad guiding bandwidth can be achieved, which are particularly important for applications with ultrashort laser pulses.

Previously, compression of 1-ps pulses from a TDL down to 250 fs and 1.6 MW of peak power [6] was achieved using this type of fiber at an overall efficiency of above 70 %, showing their large potential. Here, we demonstrate pulse compression to even shorter pulses, reaching sub-50 fs pulse duration and more than 10 MW compressed peak power. In this way, we enhanced the peak power of our TDL by a factor of > 5.

![Experimental set-up of the xenon-filled HC-PCF compression system.](image)

Figure 1: Experimental set-up of the xenon-filled HC-PCF compression system.

2. Experimental setup and results

The experimental setup is shown in Fig. 1. Our laser source consists of a SESAM-modelocked thin disk laser, generating transform-limited 860-fs pulses at 3.9 MHz repetition rate, allowing of 1.8 µJ and 7.3 W average power available.

The fiber was filled with 14 bars of Xenon from the back, the input face was left open in order to avoid stress on the fiber structure inducing damage that has been observed at high power operation in a previous experiment [6]. The fiber is a 3-ring, 7-cell hypocycloid core Kagome HC-PCF [7], and was designed for operation at our laser wavelength of 1030 nm with extremely low loss figure of 0.285 dB/m. Special care was taken to achieve negligible
dispersion at this wavelength. The measured mode-field diameter was ~30 µm. The pulses are spectrally broadened by SPM in a 2.8 m long fiber and the input power level was optimized for shortest pulse after the second order grating-compressor. We launch 1.8-µJ pulses (7.3 W of average power) with 1.9 MW peak power onto the fiber. The SPM-broadened spectrum spans over 55 nm (Fig 2a), resulting in compressed pulses with a FWHM pulse duration 48 fs (Fig 2b). The compressed average power is 4.2W, corresponding to an overall compression efficiency of 56%. The system operated stably over hours without damage.

The launch efficiency into the PCF was estimated at 86% a theoretical limitation of 94%, leading to 71% of transmission through the fiber. The output beam is linearly polarized with a Polarization Extinction Ratio of 9 dB, corresponding to a polarized transmission of 63% through the fiber with a Gaussian output beam. We used a home made decorrelation software that retrieved a peak power of 10 MW with 50% of the energy in the main peak. Further improvements of the compression setup (TOD compensation, chirped mirrors for higher efficiency, etc…) should result in a better pulse contrast and higher peak powers. Nevertheless, the achieved peak power is more than 5 times higher than that of our seed TDL.

3. Conclusion and outlook

We demonstrate multi Watt compression of a modelocked thin disk laser shortening its pulse duration below 50 fs with a peak power in excess of 10 MW. The compressed pulses were linearly polarized and the system operated stably over hours. Further optimization of the Xenon pressure and fiber length will lead to higher average power and possibly even shorter pulse durations.

This confirms the potential of Kagome-type HC-PCF for high power pulse compression. The thin disk laser technology is power-scalable, and energy levels of 41 µJ have already been achieved in 1.1-ps pulses [2]. Gas-filled Kagome-type PCFs are a promising technology for efficient compression of future 100 µJ level oscillators to the sub-50 fs regime. In the near future, we expect pulse compression at significantly higher peak and average powers exceeding 100 MW and tens of Watts respectively.

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References


GREEN MIX – THE SOLUTION FOR RELIABLE COPPER WELDING

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The reliability of copper welds is still a problem today concerning the high demands of spot or contact welding for the electronic or medical industry. Due to the low absorptivity at wavelengths of 1 micron and the very high thermal conductivity of copper, even small surface contaminations lead to drastic variations in weld quality. The wavelength of 532 nm (frequency-doubled Nd:YAG laser) is much better absorbed by copper at room temperature. Combining the two wavelengths and using the drastic increase in absorption with increasing temperature leads to an efficient spot welding solution. By the use of intelligent pulse forming with the thermal pulses of a Nd:YAG laser the spot weld reliability is improved significantly. This paper discusses a solution where Nd:YAG laser pulses composed of 85 – 90% of 1 micron and 10 – 15% of 532 nm radiation are used for spot welding of 50 – 100 micron thick copper sheets in different joint configurations (butt- and overlap-weld). The results are compared to an IR-only welding process.

1. The GreenMix technique

1.1 Superimposition of IR and Green Wavelengths

The limited reproducibility of copper welding can be improved if a 532 nm (green) laser beam is superimposed to the 1 micron (IR) laser beam. If the two free beams are focused with the same focusing lens onto the copper surface the following situation occurs.

![Figure 1. Superimposition of 532 nm (green) and 1 micron (IR) laser beam on copper surface.](image1)

The green radiation is absorbed much stronger than the IR radiation and heats up the copper surface from the center to the edge of the weld spot. As a consequence the copper temperature rises and the absorptivity of the green and IR radiation is increased. At elevated absorptivity values the influence of surface quality variations becomes less important. If a laser consists of 85% of IR and 15% of green radiation and taking into account the different absorptivities, approximately the same amount of green and IR energy is absorbed at room temperature. Thus, the total amount of absorbed energy is doubled compared to the case of an IR beam only. Since the surface of the green spot is a fourth of the surface of the IR spot, the intensities of the two beams become approximately equal in the case of an 85% IR and 15% green beam. Thus, the laser intensity incident on the copper surface is doubled compared to the case of an IR beam only. Therefore, the heating of the copper surface is speed up and the process efficiency increased.

1.2 Pulse shaping

Figure 2 depicts a typical IR pulse shape applied for spot welding with frequency conversion.

![Figure 2. Temporal shaping of the 1 micron laser pulse and resulting 532 nm frequency conversion.](image2)
At the beginning of the pulse (approx. 0.5 – 1 ms) the high intensity 1 micron radiation is partly converted to 532 nm radiation via an external frequency-doubling crystal. The 532 nm and 1 micron radiations preheat the copper surface to a level where the absorption for 1 micron radiation is high enough. The copper surface starts melting. The typical peak power during the melt phase ranges from 0.5 – 3 kW depending on the sheet thickness. Accordingly, the conversion efficiency lies between 5 – 15%. Once the copper surface starts melting, the pulse power is reduced to a level where almost no 532 nm radiation is converted. From this point on the welding is finished with the 1 micron radiation. The duration of the weld phase determines the size of the weld spot. At the end of the pulse the power is decreased steadily to influence on the metallurgical properties of the weld, i.e., its hardness.

2. Experimental results

Table 1 summarizes the results of GreenMix copper welds, compared to IR-only welds. A Rofin-Lasag SLS GX 1500 laser was used for GreenMix welds and a Rofin-Lasag SLS 200 CL8 was used for IR-only welds. Both lasers have comparable peakpower. The weld pulse shape was optimized for all configurations.

<table>
<thead>
<tr>
<th>Joint Configuration</th>
<th>GreenMix</th>
<th>IR-only</th>
</tr>
</thead>
<tbody>
<tr>
<td>Full-penetration weld 100 µm sheet</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
</tr>
<tr>
<td>Overlap joint 50 µm on 100 µm</td>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
</tr>
<tr>
<td>Butt joint 50 µm to 50 µm</td>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
</tr>
</tbody>
</table>

Table 1. Comparison of GreenMix and IR-only copper welds for different joint configurations.

The reproducibility of the weld spots made with IR-only radiation is very bad. Variations of the spot diameter and missing weld spots are observed. The weld reproducibility is clearly improved with the mixing of IR and green radiation. No missing weld spots are observed anymore. Splatter formation is significantly reduced for all joint configurations using the GreenMix technique. A pulse shape similar to the one described in Figure 2 was applied for all GreenMix weld configurations. The pulses were consisting of approximately 10 % green and 90 % IR during the melting phase.

3. Conclusions

We demonstrated a straight forward solution to increase significantly the reproducibility of laser micro-welding of copper. Using a mix of 1 micron and 532 nm radiation, applying intelligent pulse shaping, and using only one laser source not only improves the reliability of the welds, but also increases the overall process efficiency. This is a non-negligible factor in mass production of electronic components or medical devices.
1. Introduction
The laser dicing process can be used to separate dies of microsystems fabricated on silicon wafers as an alternative to mechanical sawing. With the trend of the miniaturisation of technology, microsystems become smaller and thinner and with it size-efficient separation techniques gain in importance. The qualification of laser dicing processes for dedicated applications can be done using High Resolution X-Ray Diffraction (HRXRD) methods.

2. HRXRD support in the qualification of laser dicing for Si-based microsystems

2.1 Laser dicing for microsystems
In recent years, the conventional method of wafer dicing is based on the use of diamonds blades. This technique is e.g. limited by the mechanical damaging of the material (stress, cracks) and lack of constant cutting quality but also by the lost of a remarkable part of the wafer. With respect to the growing demand for faster cutting speeds, accuracy and cutting quality, laser dicing provides an elegant die separation method approaching low strain and defect densities on the chip. In order to minimize the intrinsic HAT (heat affected zone) near the cut a careful optimization of laser processing parameters as pulse width, wavelengths or cutting speed is required. The qualification of the cut with respect to the mentioned aspects can be done by HRXRD.

2.2 HRXRD for microsystems and semiconductor devices
In defect and failure analysis, HRXRD methods are applied. This is a non-destructive tool and allows the monitoring of strain and defects mobility related to device fabrication and packaging [1,2]. Rocking Curves (RC’s) and Reciprocal Space Mapping (RSM) are carried out and monitor the crystalline quality of the Si with a very high resolution. Compared to RC’s, the application of RSM’s gives a much more detailed picture of the strain distribution and additionally about the defects on a relative scale and is therefore ideal for the here discussed study.

3. Results
First results have been obtained for 1 x 1cm chips being diced by a high-power femtosecond laser system (Fig. 1). The variation of the laser dicing parameters has consequences on the strain and defect formation and has been monitored in first studies using HRXRD. The obtained results show a strain and defect zone at the die border which varies in dependence of the chosen laser processing parameters.

Figure 1: HRXRD: a) Rocking curves carried out on the chip boarder and the center; b) Reciprocal Space Map (RSM) on the Si(004) reflection on the chip boarder; c) RSM on the chip center.

References
IDENTIFY THE SOURCE OF CONTAMINATION USING LASER OPERATIONS

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Paper describes a study for identification the source of stains on the sheet metal. The aim of the study was to determine whether the stains are contamination of external nature or they are a trace of internal corrosion. The study was carried out using a layer-by-layer removal of material by laser radiation and a LIBS-testing of the layers composition.

1. Subject
The question rose from the conflict between the manufacturer of metal fence and the customer. The fence represented steel painted sheets covered with zinc. The metal sheets were purchased by the customer and installed around the construction area. Some months later in the corner where the sandblasting machine had been working, brown stains appeared on the metal fence. The customer filed a claim for defective goods to the manufacturer. The mentioned manufacturer contacted us for the help in identification of nature of the stains, claiming that the stains appeared because of the condition of the exploitation.

2. Research
Firstly, we applied laser scaling of stains. The modes of processing were the same of laser marking. Diode-pumped Q-switched Nd:YAG-laser was used for layer-by-layer removal of the contamination. The average depth of the scaling was 10 µm.

The results showed that the very first laser shot removed the stains from the surface (Fig. 1). Hence, the source of the stains was external action.

The second part of the study was carried out by LIBS-method (laser induced breakdown spectroscopy). Elemental composition of layers was studied. Sampling from layers was implemented by consequent deepening into one path from the stain [1]. The vertical distribution of elements was observed.

The results showed that the spectral lines of Fe (iron) are strong on the upper sampling; then their intensity faded to trace; and in the third-forth sampling appeared again from the basis steel. It means that the upper layer is enriched with iron from the external source. Else, there would not be the intermediate layer without iron. Thus, in this conflict the customer complaints were unfounded.

3. Acknowledgments
The work is partially supported by State contracts 16.552.11.7027 (29.04.11) and P488 (13.05.11).
244-NM PHOTOSENSITIVITY OF PURE-SILICA FIBERS DOPED WITH BISMUTH

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Photosensitivity of a bismuth-doped silica fiber (Bi concentration <0.02 at.%) free of other dopants is investigated. UV-absorption and luminescence spectra upon 5 eV excitation are measured in the fiber preform. With the help of a frequency doubled Ar²-laser radiation (λ = 244 nm), Bragg gratings were written in both pristine and H₂-loaded fibers. The induced refractive index at a radiation dose of 150 kJ/cm² amounted to -2 × 10⁵ and -6 × 10⁵ in the pristine and H₂-loaded fibers, respectively. It is shown that the induced refractive index in the H₂-loaded fiber is highly temperature stable (~80% of the initial value retains upon annealing at temperatures of up to 1100 K).

1. Introduction
Bismuth-doped silica fibers hold much promise for the creation of fiber lasers and amplifiers in the spectral range 1150 – 1500 nm [1]. For this reason, it is interesting to investigate photosensitivity of Bi-doped silica fibers. Previously, it has been shown that Bi-doped aluminosilicate fibers are photosensitive upon exposure to pulsed radiation at 193 nm [2], as well as upon cw irradiation at 244 nm [3]. In this paper, we investigate photosensitivity of Bi-doped silica fibers free of other dopants, the Bi concentration being comparatively small.

2. Bi:SiO₂ preform and fiber properties
A single-mode fiber (cutoff wavelength ~ 1.1 μm) was fabricated at FORC by the powder-in-tube (PIT) technique (the fabrication procedure was described in [4]). The fiber had a fluorosilicate inner cladding and undoped-silica outer cladding, the core-cladding index difference being ~9×10⁻⁶. The fiber refractive index profile is shown in Fig. 1. The core chemical composition was determined with the help of a scanning electron microscope with an X-ray spectrometer analyzer (Oxford Instruments JSM 5910LV). The bismuth concentration in the core proved to be lower than the detection threshold (~0.02 at.%).

![Image](image1.png)

Figure 1. Refractive index profile of the Bi:SiO₂ fiber.

![Image](image2.png)

Figure 2. Optical absorption, luminescence and 3.1-eV luminescence excitation spectra.

Fig.2 shows the absorption spectra measured in the core of the fiber preform slice in the range 2.5 – 6.5 eV [4]. On the background of the short wavelength absorption, a band with a maximum at 5.45 eV is seen, its FWHM being 0.88 eV. Such a band is observed in Bi-doped glasses of various composition and has been attributed to Bi³⁺-ion absorption [5]. Note that the short wavelength absorption and the above band do not occur in pure silica glass fabricated by the PIT-technique. Fig.2 also shows a luminescence spectrum measured at room temperature upon 5-eV excitation. This spectrum consists of two bands: 3.17 eV (FWHM=0.4 eV) and 4.3 eV (FWHM=0.6 eV). The parameters of these luminescence bands proved to be close to those of the triplet and singlet luminescence bands of the germanium oxygen deficient center (Ge-ODC) [6], despite the absence of germanium in the samples. Note that the absorption band maximum does not coincide with the 3.17-eV luminescence excitation band maximum (dotted line in Fig.2). Interpretation of the absorption and luminescence bands observed calls for further study; however, we believe them to be associated with three-fold-coordinated Bi atoms with two unpaired electrons. Recall that two-fold-coordinated Ge and Si atoms (Ge-ODC and Si-ODC) also possess two unpaired electrons.
3. Bi:SiO₂ fiber photosensitivity and induced index annealing

The presence of a UV absorption band allowed us to assume that the Bi:SiO₂ fiber is photosensitive by analogy with the known fact that photosensitivity of germanosilicate glasses is due to Ge-ODC [7]. We did succeed in writing fiber Bragg gratings (FBGs) in this fiber by using cw frequency-doubled Ar⁺-ion laser radiation (244 nm) and a Lloyd interferometer, the writing power density being 30 W/cm². Note that the substrate tube material was transparent to the UV radiation, whereas the absorption in the fiber core was as great as ~5 dB/mm. The latter provided absorption of the incident light in the fiber core on the level of 1%. FBGs length was 6 mm. In this way FBGs were written in the Bi:SiO₂ fiber and, for comparison, in the Corning SMF-28e fiber (3.5 mol.% GeO₂), in both pristine and H₂-loaded fiber pieces. For the Bi:SiO₂ fiber and the H₂-unloaded SMF-28e fiber, the integral irradiation dose was 150 kJ/cm², and for the H₂-loaded SMF-28 fiber, only 20 kJ/cm² owing to its higher photosensitivity.

The refractive index (RI) modulation in the FBG written in H₂-free fiber amounted to ~1×10⁻⁵ (the induced RI ~2×10⁻⁵). H₂ loading increased photosensitivity of the Bi:SiO₂ fiber: at the same UV dose the RI modulation amounted to ~3×10⁻⁵ (the induced RI ~6×10⁻⁵). Note that the H₂-loading effect was not as strong as in the case of germanosilicate fibers.

To measure thermal stability of the induced RI, we placed the FBGs in an oven, its temperature increasing at a rate of 0.25 K/sec. During the annealing, the FBG reflection spectrum was measured at equal time intervals of 30 s with the help of an ANDO-6317B spectrum analyzer.

![Figure 3](image_url)

Fig.3 shows the evolution of the normalized integrated coupling coefficient (NICC) in the course of FBG annealing. One can see two annealing bands at ~550 and ~950 K in the H₂-free Bi:SiO₂ FBG. In the H₂-loaded Bi:SiO₂ FBG, the low-temperature annealing band features the same characteristics, whereas, in contrast to the unloaded FBG, most of the induced refractive index (~80%) possesses a very high thermal stability, which retains at temperatures of up to 1100 K. Note that the annealing results obtained in this paper agree well with those of paper [2], in which the induced index thermal stability was investigated in a Bi:Al SiO₂ fiber irradiated at 193 nm. This fact testifies that refractive index induction in Bi-doped silica fibers with and without aluminum is due to similar physical mechanisms. Further details will be reported at the Conference.

In conclusion, we acknowledge with thanks fruitful discussions with Dr. A.L. Tomashuk.

References

High average power, high repetition rate ultrafast lasers with µJ pulse energies are increasingly used for biomedical and material processing applications. Interesting applications for the ultrashort pulse laser systems are in the field of selective structuring of thin-films. Thin-film solar cells have shown a huge potential to decrease cost of manufacturing for photovoltaic generation. Despite many research attempts to optimize materials the mass production of thin-film solar cells is still looking for versatile tools for the structuring of the thin-film coated area, where thin films with a thickness of ca. 1 µm have to be line structured with galvanic separation without damaging the substrate or any other layers. In this work we report on study of the selective structuring of thin Boron (B) doped ZnO film with femtosecond (fs) and picosecond (ps) laser pulses. Experimental data on the removal threshold energies of thin ZnO film as a function of pulse width and number of laser pulses per position will be presented. Based on the experimental finding mechanisms of direct and induced ablations in fs- and ps- regimes can be derived.

1. Introduction

Transparent conductive oxide (TCO) thin films are widely used in manufacturing of both flat panel displays and solar cells – two market segments which have been rapidly developing in the last decade. TCO thin films allow the electrical contacting of large active areas and are largely transparent in the visible spectral range.

In order to use the TCO films in flat panel displays and solar cells it is usually necessary to pattern them for creating a special functionality. Laser writing offers a flexible process that allows easy change of the structured pattern and can be used for large substrates, like thin film photovoltaics panels [1, 2]

![Figure 1: Direct (a.) and induced (b.) ablation.](image)

Thin-film photovoltaic panels require sectioning into multiple cells which are connected in series because otherwise they would form low voltage, high current devices, with high ohmic losses. Typically the panels are structured to more than hundred cells to achieve a current-voltage characteristics suited for high energy extraction. The three scribing patterns P1, P2 and P3 form the integrated circuits for cell connection on the module [2, 3].

Boron-doped zinc oxide (ZnO) films deposited by low pressure chemical vapour deposition on a glass substrate has shown to be an ideal candidate for micromorphous silicon thin film solar cells [4]. In this work we report on a study of the selective structuring of thin B-doped ZnO film with femtosecond and picosecond laser pulses at 1040 and 1064 nm, respectively. The two structuring techniques i.e. direct (Fig. 1a) and induced (Fig 1b) ablation are examined for this purpose.

2. Experimental Setup and Materials

2.1 Laser source

The laser-structuring of B-doped ZnO thin films [4] deposited on the glass substrate was performed in the application laboratory at High Q Laser GmbH, Austria. The two near-IR ultrafast lasers from High Q Laser GmbH were used in this work. The first one is a commercial Spirit™ laser system which is based on a Yb-doped chirped pulse regenerative amplifier with pulses as short as 350 fs at 1040 nm. An average power of 2, 4 and 8 W is achievable all within the same compact housing. Additionally, single pulse and burst energies can be dialed freely without the usual first pulse effects. The second one is picoREGEN UC with the average power of 30W at the fundamental wavelength 1064 nm. Both lasers have a very good beam quality factor M² <1.2. The intensity of the beam was adjusted with an integrated fast (300 kHz) acousto-optic beam attenuator.
2.2 Sample preparation
The Boron-doped ZnO films of ca. 1.5 µm thickness deposited on glass substrate were prepared by means of low pressure chemical vapor deposition technique. The TCO samples studied in this work were produced using an OC Oerlikon TCO 1200 system [4].

3. Results and Discussion
3.1 Single and multiple pulse process thresholds.
The single and multiple pulse laser fluence process thresholds can be determined as the minimum average laser fluence required to remove the complete TCO layer with a single or with multiple laser pulses, respectively. For a Gaussian spatial beam profile the process threshold $F_{th}^P$ can be obtained from the relationship between the laser fluence $F$ and the diameter $D$ of a crater produced by laser pulses [5].

3.2 Process threshold values.
Laser ablation is usually driven by absorption and heat transport with subsequent melting and evaporation of the illuminated material. Thus, for direct laser ablation the removal process is driven by thermodynamical phase transitions with a combined change of pressure and volume (direct ablation, Figure 1a). The behavior is different if the laser pulses are applied from the side of a transparent substrate (induced ablation, Fig. 1b). The observed ablation processes are not purely governed by thermal effects (heating, melting and evaporating) of the TCO layer, but are rather induced by the absorption of laser energy at the TCO/glass interface. The absorption of the laser pulse creates a high pressure vapor bubble which then lifts off the film. Hence, we call that ablation mechanism “induced laser ablation”.

![Diagram](image)

Figure 2: Process threshold fluence for a TCO layer deposited on a glass substrate for direct (black, triangles), induced (red, squares) laser ablation and punching fluence (green, squares) for induced laser processing as a function of the number $N$ of femtosecond (left) and picosecond (right) laser pulses per location.

Figs. 2 depict the laser threshold fluence for complete ablation of a 1.5 µm thick B-doped ZnO layer on glass substrate using the femtosecond (left) and picosecond (right) laser pulses by means of direct and induced ablation. Our study shows that the application of the laser pulses from the glass side for the structuring of thin transparent layer leads to non-thermal selective removal of the film at energies significantly lower than the energies necessary for liquefaction and evaporation. For direct laser ablation “pre-pulses” were necessary to initiate the ablation of the TCO layer using both femtosecond and picosecond laser pulses. Interestingly, the application of laser pulses with different pulse durations (350 fs and 10 ps) leads to a significant difference in the process thresholds. This is evidence for the different mechanisms involved in the removal of the TCO layer with the laser pulses at 350 fs and 10 ps. The mechanisms of direct and induced ablations in fs- and ps- regimes derived from our experimental finding will be presented.

4. Acknowledgments.
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References
Optimized ablation efficiency with ultrafast lasers on metal

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Abstract
High power picosecond lasers enable micro machining of metals, semiconductors, dielectrics and glass resulting in a combination of high quality, yield and throughput. During the last few years ultrafast lasers have become established tools for the Semiconductor, Photovoltaics, Automotive and Flat-Panel-Display industries. The exploited average powers range from 100 W at 1030 nm to 60 W at 515 nm. Pulse durations in the range of a few picoseconds avoid thermal effects that are typically associated with nanosecond lasers. Laser wavelengths are chosen in respect to absorption properties of the material to be processed; wavelengths of 1030 nm, 515 nm and 343 nm are being used.

In order to reach high quality results when processing materials with ultrafast lasers it has to be considered that the fluence chosen for the process have to be between the ablation threshold and the thermal threshold. The optimum is reached when the ablation threshold isophote reaches its maximum width. Defocussing allows to reach this optimum where maximum ablation efficiency comes along with minimum heat influence on the workpiece.

1. Content

In this work isophotes of gaussian beams of an infrared picosecond laser are discussed. Isohotes are used here as a criteria for an optimum working point regarding the z position of the workpiece in respect to the gaussian laser beam – defocussing is considered as a powerful parameter to optimize ablation efficiency and quality. Fig. 1 shows an example of a calculated isophote and the effect on a workpiece. Fig. 2 shows the calculated isophotes for ablation threshold and thermal threshold on stainless steel.

Ablation rates for stainless steel as a function of the focal position are provided.

References
THE STUDY OF TM:SC₂SIŌ₅ CRYSTAL LASER PUMPED AT 1678 NM.


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The Tm³⁺:Sc₂SiO₅ laser crystal was grown and experimentally investigated. Lasing of this crystal at 1.98 um under the pumping into the absorption line ³H₄ – ³H₆ of Tm³⁺ ions was realized.

It was experimentally shown in [1] that Tm³⁺:Sc₂SiO₅ (Tm:SSO) crystal can be used for lasing in 2 micron range under pumping at 795 nm. In the present work, we realized and studied for the first time the lasing in a Tm:SSO crystal pumped at 1678 nm by a Raman shifted Er-fiber laser corresponding to the absorption line of the ³H₄ – ³H₆ laser transition of Tm³⁺ ions [2].

Biaxial Tm:SSO crystal have been grown by the Czochralski method from an iridium crucible 4 x 4 cm. The concentration of Tm³⁺ ions was ~ 5%. Laser active element was cut out in the form of a cube with ~ 3.5 mm edges. The uncoated polished two pairs of plane-parallel faces of the cubic crystal were oriented along crystallographic orientations < 100 >, < 010 >. Active element was cooled by a contact with copper heat sink at room temperature. Laser cavity was formed by flat mirror and 52 mm radius of curvature output coupler with 97% reflectivity. Length of laser cavity was about 52 mm. Diameter of spot size of focused in crystal pump beam was about 80 um.

![Fig.1. Output power vs. absorbed pump power.](image)

The results of experimental investigations of Tm:SSO laser output power vs. absorbed pump power at 1.678 um are shown in Fig.1. Laser demonstrates slope and total efficiencies ~ 42% and ~ 30% respectively at output power up to ~ 300 mW under pulsed pumping (10 Hz pulse repetition rate and 1.4 duty cycle). The analysis of experimental results has shown that the further improvement of Tm:SSO laser efficiency is possible on the way of improvement of laser crystal quality.
The absorption and luminescence spectra for different orientations of Tm:SSO crystal were measured.

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References

GROWTH PECULIARITIES AND NON-LINEAR PROPERTIES OF PROFILED DOPED STRONTIUM-BARIUM NIOBATE CRYSTALS

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Abstract
Sr$_x$Ba$_{1-x}$Nb$_2$O$_6$ (SBN) crystals are well-known photorefractive and non-linear materials. SBN doping with rare-earth and transition metals allows to operate the crystal properties. The present investigation is directed on obtaining of high-homogeneous pure and doped with Ce, Cr, Co SBN crystals by modified Stepanov technique and studying their non-linear properties. The growing technique provides high optical quality of single crystals: absence of convective and rotation growth striations, inclusions and other inhomogeneities of chemical composition. The specific features of the technique were studied and growth conditions for obtaining SBN crystals in bulk-profiled configuration were optimized.

The photorefractive and non-linear properties of SBN pure and doped with Ce, Cr and Co were investigated. Two-wave mixing scheme and a continuous single-mode He-Ne laser as a source of coherent radiation were used for the grating recording. It was shown that SBN:Ce crystal is an excellent medium for high efficiency holographic information recording. SBN:Cr and SBN:Co crystals are promising photorefractive materials with short response time. The as-grown SBN crystals were also used to demonstrate the diffuse noncollinear second harmonic generation emitted by a random domain SBN structure and Stimulated Raman Scattering and two-photon absorption associated with cubic nonlinear susceptibility of the materials.

1. Introduction

The search of new non-linear materials and development of technologies for producing an optically perfect crystals remain actual up to now. Among solid-state materials an important role play ferroelectric crystals of strontium-barium niobate solid solutions Sr$_x$Ba$_{1-x}$Nb$_2$O$_6$ (SBN:x), which belong to a class of active dielectric, exhibiting qualitatively new properties under influence of external factors. SBN single crystals are characterized by the extremely large electro-optical coefficients and high nonlinear optical properties. Doping of the SBN solid solutions by rare-earth and transition metals allows to operate the properties of the crystals and create new materials for different applications, particularly in the areas of pyroelectricity, piezoelectricity, electro-optics, photorefractive optics and non-linear optics.

The present investigation is directed on obtaining of high-homogeneous pure and doped with Ce, Cr, Co SBN crystals and studying their photorefractive and non-linear properties.

2. Crystal growth

Choice of growth method was determined by the possibility to obtain from the melt the crystals the required size and quality with reproducible characteristics. SBN:x is a solid solution with wide homogeneity range 0.25 ≤ x ≤ 0.8. Introduction into the matrix doping ions of different type and concentration causes difficulty to obtain crystals given compositions and high optical quality using the traditional Czochralski method. We showed the possibility to obtain the crystals from the melt by the modified Stepanov technique using special die of capillary type. This growing technique provides: high optical quality of single crystals, free of growth striations, inclusions and other inhomogeneities of chemical composition; definite cross-section and sizes of growing of single crystalline rods [1]. The specific feature of the Stepanov technique is that the melt is transported via a feed capillary to the meniscus on the top plane of a die. It is assumed that there is no convective mixing of the melt in the capillary- no convective striations in as-grown crystal. Profiled crystals were grown without rotation – no rotation striations in as-grown crystals. The form and size of the bulk-profiled crystals are defined by the character of the top plane of a die. It is assumed that there is no convective mixing of the melt in the capillary- no convective striations in as-grown crystal. Profiled crystals were grown without rotation – no rotation striations in as-grown crystals. The form and size of the bulk-profiled crystals are defined by the character of the top plane of a die. Nominally pure single SBN crystals of different composition (x = 0.61; 0.75) have been grown as well as ones doped with Ce, Cr or Co ions. Doping ions were introduced into the matrix (congruently melting SBN:61) in the form of oxides. Crystal growth parameters such as temperature gradients in thermal cell, volume crystallization rate, time and temperature of annealing processes were optimized for crystals of different chemical composition. The crystals (14x24mm) in cross-section and up to 80 mm in length were grown.

The control of optical quality of the crystals was performed by optical and polarization-optical methods, laser radiation scattering control. The method of dynamic holography was used for investigation of real structure of as-grown crystals. The method allows to carry out the high-speed monitoring of the presence or absence of phase inhomogeneities in the bulk of large single crystals with minimum mechanical treatment of crystal surfaces.
3. Photorefractive properties

Bulk-profiled SBN crystals have a high optical quality and reproducible photorefractive characteristics. The photorefractive properties of pure SBN and SBN crystals doped with Ce, Cr and Co were studied. A continuous single-mode He-Ne laser as a source of coherent radiation for the grating recording was used. The gain coefficients and response times were measured in two-wave mixing scheme. It was shown that SBN crystal doped with Ce is an excellent medium for high efficiency holographic information recording. SBN crystals doped with Cr and Co are promising photorefractive materials with short response time. The values of the half-wave voltage were measured depending on type and concentration of doping ion. The electrooptical coefficients were calculated for all doped crystals. The properties of the crystals are summarized in the table 1.

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Dopant concentration wt.%</th>
<th>K_{eff}</th>
<th>α_{0.5}</th>
<th>T_{max}</th>
<th>λ_{max}</th>
<th>r_{33}</th>
<th>Ls</th>
<th>τ</th>
<th>N_{eff}</th>
<th>ω/ cm</th>
<th>α_{2}</th>
<th>10^{12}</th>
<th>μtr</th>
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<tr>
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<td>0.002</td>
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</table>

K_{eff} – effective segregation coefficient; U_{0.5} - half-wave voltage; r_{33} – electrooptical coefficient; Γ – two-wave mixing gain; τ – response time; α – absorption coefficient; T_{max} – Curie temperature; L_{s} – Debye screening length; N_{eff} – effective concentration of carrier traps; ω/σp – ratio of electron and hole conductivities; σd – dark conductivity; μtr – product of the mobility and the recombination time of charge carriers.

4. Non-linear properties

The distinctive features of the material include the presence of domain structure – set of domains with different polarization vector orientation. Nanoscale domain structures in SBN crystals have been studied using an atomic force microscopy (AFM) [2]. SBN crystals are presented an attractive object for experimental research ferroelectric processes at micro- and nanolevels and for "domain architectures" in the field of AFM probe. The examples of regular domain structures for using crystals as non-linear elements for conversion laser radiation were shown.

The as-grown SBN crystals were also used to demonstrate the Stimulated Raman Scattering (SRS) [3] and two-photon absorption (2PA) [4] as physical phenomena associated with cubic nonlinear susceptibility of the materials. The two-photon absorption coefficients were determined as 0.17 – 0.31 cm/GW depending on laser beam polarization, type and concentration of doping ion. Relatively low values of 2PA coefficients and steady-state Raman gain coefficient (0.42 cm/GW) result from low cubic nonlinear susceptibility of SBN crystals.

References
**Abstract**

Power Scaling of a Q-switched laser ready for internal frequency conversion by time-multiplexing scheme is demonstrated by using single crystal photo-elastic modulator. The design is based on combining two Nd:YVO4-gain-channels.

1. **Introduction**

The need for high processing speed in material processing in many areas of the micro-electronic and photovoltaic industry constantly requires scaling average output power. It is usually important that higher processing speed is achieved with unchanged pulse parameters what leads to requirement that the average power and repetition rate have to be scaled simultaneously.

As an alternative we proposed and demonstrated solution for power scaling based on a dual channel resonator. Several dual channel configurations having single active medium have already been proposed, mostly for measuring application [2,3]. Further several configurations are proposed based on one or two gain mediums for the generation of special tailored laser pulses for micro-processing [4]. Furthermore a configuration based on dual channel resonator and a single electro-optical modulator (EOM) was proposed [5] for power and repetition rate scaling. Role of the EOM was to Q-switch both channels in turn. As a result repetition frequency and power were doubled. The main deficiency of such setup is due to EOM itself as it requires a high voltage for driving (kV range).

Our approach is based on the combination of two channels and two gain mediums. We use a time-multiplexing scheme [6]. The basic idea is that the original single channel resonator is upgraded to two channels. However, in principle each single channel has the same structure and therefore the same optical properties as the original resonator. The Q-switching is carried out by one acousto-optical modulator in the common part of the resonator. Switching between the two channels is performed with a Single Crystal Photo-Elastic Modulator (SCPEM, [6-8]) that is suitable for high frequency operation and requires just a few volts for driving.

2. **Experimental setup**

The setup is based on a standard industrial Q-switch laser that is originally designed for intra-cavity frequency up conversion. It was upgraded by adding an additional channel to the resonator with its own gain medium and pumping system. Fig. 1 shows the adapted setup.

![Fig 1. Experimental setup](image)

3. **Results**

Table 1 shows an overview of the pulse parameters and the average power for a repetition rate from 20.5 KHz to 61 KHz for single channel operation or 41 kHz to 122 kHz for dual channel operation. In the table the average and peak output power for the single and dual channel laser are presented respectively. Due to additional optical components inserted into resonator an efficiency of approx 90% in each channel was achieved, therefore the power was increased by 80%.
Table 1. Laser pulse parameters of dual channel laser for four highest repetition rate of the SCPEM with a resonance frequency of 91.5 KHz and setup without λ/4 plate.

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<th>Single channel repetition rate (KHz)</th>
<th>Single channel: Average power (W)</th>
<th>Single channel: Peak power (KW)</th>
<th>Dual channel repetition rate (KHz)</th>
<th>Average power Ch1+Ch2 (W)</th>
<th>Peak power (KW)</th>
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</thead>
<tbody>
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4. Conclusion

The concept of power and repetition rate scaling of a Q-switched solid state laser consisting of a two channel resonator were successfully demonstrated. The simplicity of the setup allows for easy application to almost every kind of laser. One disadvantage, however, is the fixed multiplexing frequency which allows only certain pulse repetition frequencies. In principle the concept also allows further scaling of the power and repetition rate. For example each of the two channels can be further split into two parts by introducing an additional polarizer and modulator.

Acknowledgements

Part of this work was supported of the EU funded FP7 ALPINE Project, n. 229231.

References


We present an ultra-broadband femtosecond laser source operating in the mid-infrared. Our approach is to generate the mid-infrared (MIR) radiation by optical parametric amplification (OPA), using a commercial femtosecond seed laser at 1.56-µm and an industrial-grade 12-ps pump laser at 1.064-µm. The spectral phase of the MIR idler output pulses can be manipulated with a pulse shaper placed in the near-infrared (NIR) seed beam path. With this system we achieve clean 75-fs (110-fs) pulses with energies of 7 µJ (14 µJ) at a repetition rate of 100 kHz (50 kHz) around 3.4-µm center wavelength.

1. Introduction

We report on an ultra-broadband, optical parametric chirped-pulse amplification (OPCPA) system operating at 3.4 µm center wavelength. The system delivers clean pulses as short as 75 fs or 110 fs with record-high 700 mW average power at repetition rates of 100 kHz and 50 kHz, respectively. Corresponding pulse energies of 7 µJ and 14 µJ are achieved. The amplification occurs in a collinear two-stage amplifier based on apodized, aperiodically poled Mg:LiNbO₃ (APPLN) [1, 2]. The use of apodized linearly chirped quasi-phasematching gratings enables us to maintain a smooth spectral phase of the output pulses while reaching 45 dB of single-pass gain [3, 4]. The spectral phase of the mid-infrared output pulses can be manipulated with a pulse shaper placed in the near-infrared seed beam. The seed spectral phase is then transferred to the idler during the optical parametric amplification (OPA) process.

2. The APPLN optical parametric amplifier

A commercially available mode-locked femtosecond fiber laser operating at λ = 1.56 µm is used to seed the OPCPA with 87 pJ of pulse energy. The seed pulse is stretched to approximately 2.6 ps by a 2-prism stretcher and a SLM (spatial light modulator) pulse shaper [6] and subsequently sent into the first amplifier stage. The pump source is an industrial laser (Time-Bandwidth Products Inc., Duetto) operating at λ = 1.064 µm and delivering 12-ps pulses at a repetition rate of 100 kHz (50 kHz) and average output power of up to 11 W. A fraction of the output of this laser is further amplified by a Nd:YVO₄ slab amplifier [7] to an output power of 46 W. A phase locked loop (PLL) stabilizes the pulse train of the pump laser to the pulse train of the seed laser with a timing jitter of less than 150 fs rms. The delay between pulses of the seed and pump oscillator can be adjusted within ±1 ns by setting the phase of the PLL. Pump and seed beams are collinearly overlapped in the first and second OPA stage.

Figure 1: Temporal pulse shape (solid blue line) and phase (dashed red line) after amplification in a poling-period apodized APPLN amplifier as reconstructed with SHG-FROG [5]. At 50 kHz (a) we achieve pulse durations of 110 fs whereas at 100 kHz (b) slightly shorter 75 fs pulses could be realized. By the use of an apodized APPLN grating, we maintain a smooth spectral phase during amplification resulting in clean high-peak-power pulses. (c) The non-uniform QPM grating structure implemented in the amplifier crystal.

Figure 2: Setup of the MIR source. The 1.5 µm signal beam is stretched by a SLM pulse shaper and a prism stretcher before seeding the OPCPA. The MIR idler is extracted only after the second amplification stage. By propagation through 150 mm Si with a transmission of 90% compression to 75 fs (100 kHz) or 110 fs (50 kHz) is achieved.
At 100 kHz repetition rate we use 8 W and 30 W to pump the first and the second amplifier stage corresponding to intensities of 6.8 GW/cm² ($r_{1/2} = 250 \mu$m) and 9.4 GW/cm² ($r_{1/2} = 400 \mu$m), respectively. The corresponding values for 50 kHz repetition rate are 8 W and 24 W resulting in intensities of 13.6 GW/cm² ($r_{1/2} = 250 \mu$m) and 8.5 GW/cm² ($r_{1/2} = 550 \mu$m), respectively. In both stages a 10-mm-long APPLN chip with transverse dimensions of 1 x 6 mm and a chirp-rate of $\kappa = -250 \text{ cm}^{-2}$ is used to achieve a broad phase-matching spectral window ranging from 2.71 to 4.24 μm. Our compressor consists of two rods of AR-coated bulk silicon with a total length of 150 mm and a total transmission of 90%. We were able to recompress the 3.4-μm-pulses to 75 fs duration with 7 µJ pulse energy (or 110 fs and 14 µJ at 50 kHz repetition rate) (Fig. 1). A schematic overview of our setup is shown in Fig. 2.

3. Conclusion and outlook

In conclusion, we have demonstrated a state-of-the-art femtosecond OPCPA system operating in the mid-infrared with record-high average output power. The used gain structures also represent the first practical implementation of poling-period-apodization in the context of a high-power OPCPA based on APPLN. With the use of APPLN one can overcome the bandwidth limitations of conventional PPLN in collinear OPCPA configurations [8]. Spectral ripples and temporal pre-pulses are well suppressed by this method. This allows amplification of few-cycle pulses with a clean temporal structure holding most of the energy in the main pulse. An upgraded seed source with matched QPM designs will allow us to fully use the amplification bandwidth of the amplifier and extend the currently seed-limited performance to significantly shorter pulses.

References

ZERO-DISTANCE PULSE FRONT OF STRETCHER AND ZERO-DISTANCE WAVE FRONT OF ITS OPTICAL SYSTEM

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Abstract

A two-grating stretcher is a dispersion delay lines which is widely used in the chirped-pulse amplifier. The dispersion of the stretcher can be described by using the concept of “zero-distance pulse front”. Note that aberrations of the optical system of the stretcher can be characterized by using the concept of “zero-distance wave front”. The similarity of these descriptions allows us to study the influence of aberrations of the optical system on dispersion of stretcher.

To gain ultra short laser pulses (USPs) the method of the chirped-pulse amplification (CPA) is used. In this method the duration of the input transform-limited USP is stretched by using a dispersion delay lines (DDL) with positive dispersion before optical amplification. By lengthening the duration of the pulse, energy can be efficiently extracted from the gain medium, while avoiding damage to the optical amplifier. After optical amplification, when the pulse is very energetic, the DDL with negative dispersion is used to “recompress” the pulse back to its original duration. As the positive and negative DDLs for CPA are now widely used two grating Martinez’s stretcher [1] and two grating Treacy’s [2] compressor, respectively. In grating delay lines the group delay $T(\lambda)$ for a monochromatic wave of wavelength $\lambda$ is proportional to the optical path length $p$ of its trajectory: $T(\lambda) = p(\lambda)/c$; where $c$ is the speed of light in vacuum [1-4].

The Treacy’s compressor consists of a pair of identical reflection gratings arranged parallel to each other [2]. The Martinez’s stretcher consists of a pair of identical reflection gratings and a perfect optical system between them [1]. Martinez’s and Treacy’s systems are closely interrelated. Actually, when the second grating $G_{Mar2}$ is shifted along the optical axis, then the image of the first grating $G_{Mar1}$ and the second grating $G_{Mar2}$ form the so-called “virtual Treacy’s system” [3-6] in the image space of the optical system.

In [4,6] using the unfolding technique we have shown that the natural visual graphic characteristic of DDLs (such as virtual Treacy’s compressor or Martinez’s stretcher) is the “zero-distance pulse front” (Fig. 1). The sum of the zero-distance pulse front $T_{Mar}(\Delta \xi)$ of Martinez’s stretcher and the zero-distance pulse front $T_{Vir.Tr}(\Delta \xi)$ of virtual Treacy’s system equals the time traveling from the point $Q$ to the point $Q'$ along all ray paths traversing the perfect optical system $T_{Opt.sys}$ [3-6]:

$$T_{Mar}(\Delta \xi) + T_{Vir.Tr}(\Delta \xi) = T_{Opt.sys} \quad (1)$$

In spatial chirp of the stretcher $\Delta \xi(\lambda)$ is the displacement of a light ray with wave length $\lambda$ from the axis of this chirp (Fig.1).

It was shown in papers [3,7,8] that dispersion of the stretcher depends on aberrations of its optical system. As that the aberrations of a real optical system can be characterized by its “zero-distant wave front” $\{Q,M(\Delta \xi)\} = \text{optical path length } [Q,M(\Delta \xi)]$ we investigated the relationship between the zero-distant wave front of the stretcher and the zero-distant wave front of its optical system (Fig. 1). In the case of Martinez’s stretcher with a real optical system the formula (1) takes the form

$$T_{Mar}(\Delta \xi) = |Q,M(\Delta \xi)/c| - |Q,M(\Delta \xi)/c - M,M/c|.$$
Fig. 1.

References:
CONTROL OF SPECTRAL PARAMETERS IN VANADIATE LASERS

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Spectroscopic and lasing properties of Nd:GdVO$_4$, Nd:GdVO$_4$, and mixed Nd:Y$_x$Gd$_{1-x}$VO$_4$, Nd:Y$_x$Sc$_{1-x}$VO$_4$ crystals were investigated. We have experimentally investigate, for the first time as far as we know, angular dependences of the luminescence intensity of Stark transitions in vanadate crystals. The frequency shift and redistribution of the luminescence intensity of Stark transitions are observed. We suggest using combinations of two different vanadate crystals to creation active media with new parameters. New wavelength of laser generation, spectrally tunable radiation, two-color lasing were realized.

Here, we present laser sources based on a novel methods control of spectral parameters in diode-pumped vanadate lasers. Nd:GdVO$_4$, Nd:GdVO$_4$, and mixed Nd:Y$_x$Gd$_{1-x}$VO$_4$, Nd:Y$_x$Sc$_{1-x}$VO$_4$ vanadat are an excellent laser crystals. This crystals are ideal laser host materials for the flash-lamp and diode pumped solid state lasers as its good physical, optical and mechanical properties. The $a$-cut (σ-polarization) and $c$-cut neodymium-doped vanadate crystals are efficient active media and have a considerable potential to produce new laser possibilities [1-3].

Spectroscopic and lasing properties of Nd:GdVO$_4$, Nd:GdVO$_4$, and mixed Nd:Y$_x$Gd$_{1-x}$VO$_4$, Nd:Y$_x$Sc$_{1-x}$VO$_4$ crystals were investigated. We have experimentally investigate, for the first time as far as we know, angular dependences of the luminescence intensity of Stark transitions in vanadate crystals. The frequency shift and redistribution of the luminescence intensity of Stark transitions are observed. We suggest using combinations of two different vanadate crystals to creation active media with new parameters.

Luminescence spectra at the $^{4}F_{3/2}$–$^{4}I_{11/2}$ transition for $a$-cut (σ-polarization) and $c$-cut Nd:YVO$_4$, Nd:GdVO$_4$, Nd:Gd$_{0.7}$Y$_{0.3}$VO$_4$, and Nd:Sc$_{0.03}$Y$_{0.97}$VO$_4$ crystals illustrate the widening of the spectral line. Such broadened luminescence bands allow to realize new functionalities of lasers based on $a$-cut (σ-polarization) and $c$-cut neodymium-doped vanadate crystals such as: new wavelength of laser generation, spectrally tunable radiation, two-color lasing, generation of sub picosecond pulses.

We have shown that lasers with no selective resonator based on $a$-cut for $\pi$- and $\sigma$- polarized vanadate crystals) work at difference wavelengths. The different wavelength for $\pi$- and $\sigma$- polarizations allows creating two-color lasers with orthogonal polarization, which is important for the conversion to terahertz spectral range using the GaSe nonlinear optical crystals as converter for example.

Two-color lasing has been obtained in the $a$-cut ($\pi$- and $\sigma$-polarization) and $c$-cut vanadate crystals at the spectral lines separated by 2.3, 3.2 and 3.8 nm with parallel and orthogonal polarization. QW, mode-locking and Q-switching regimes with passive and active acoustic-optical modulators were realised for two-color lasers. The grazing incidence multipass amplifier based on 1 at.% $c$-cut Nd:YVO$_4$ slab (dimensions: 20 mm × 5 mm × 2 mm) was used for the amplifier two-color radiation with parallel and orthogonal polarization.

References
Abstract:

We present continuously tunable Vertical External Cavity Surface Emitting Lasers (VECSEL) in the mid-infrared. They emit a single longitudinal mode, which is shifted modehop-free over a broad wavelength region (>100 cm⁻¹) at constant temperature and constant pump power. The optically pumped VECSEL are based on IV-VI semiconductors, the active layer consists of PbSe QW in Pb₁₋ₓSrxSe host material. By varying the QW thickness a total wavelength range from 3 – 5 µm is covered with thermo-electrical stabilization. The structure of the laser is comparably simple and consists in total of less than 50 layers. Due to favorable laser characteristics like sufficient output power, narrow linewidth and a modehop-free tuning range this laser type is very well suited for spectroscopic applications.

1. Introduction

For gas-sensing the mid-infrared (MIR) wavelength region (~ 3 – 10 µm) is highly interesting due to strong absorption lines of many gases. Thus large efforts have been made in developing suitable laser modules. Aside the required emission wavelength lasers for spectroscopic applications should fulfill additional requirements like narrow linewidth, sufficient output power, thermo-electrical stabilization and a broad and continuous tuning range. A broad tuning range leads to a much better selectivity and robustness against possible interfering gas species. It also allows the measurement of a set of multiple target compounds and to analyze gas mixtures with a single laser.

We present continuously tunable VECSEL in the MIR, which fulfill all of the listed requirements. They emit a single emission mode, which is tuned modehop-free over more than 100 cm⁻¹ at constant temperature and constant pump power. In the following the setup and the characteristics of our lasers are described.

2. Technology

The lasers are based on IV-VI semiconductors like PbTe, PbSe and alloys thereof. Due to the given bandgap energy of this semiconductor class VECSEL emitting from below 3 µm to 10 µm have been realized, with a maximum operation temperature of 60°C in pulsed mode [1,2]. The continuously tunable VECSEL presented here are emitting from 3 to 5 µm [2] and the schematic structure is shown in Fig. 1.

![Figure 1: Schematic setup of the modehop-free tunable VECSEL](image-url)
The curved Bragg mirror is mounted in a distance of < 100 µm and consists of 5 to 6 quarter-wavelength pairs of Si/SiO or Si/SiO₂. The VECSEL is optically pumped on axis through the top mirror. As pump source a diode laser or a fiber laser with 1.55 µm emission wavelength is used. The generated laser light is emitted through the bottom mirror. The total structure contains not more than 50 layers and no complicated after-growth process steps are needed. This shows the simplicity of our laser technology.

Due to the short cavity-length only one longitudinal mode is amplified resulting in monomode emission. By moving the external mirror via a Piezoelectric crystal this single mode can be tuned modehop-free over a broad wavelength range. The width of this range depends on the gain-width and the free spectral range. Up to now tuning over 100 cm⁻¹ has been achieved at constant temperature and constant pump power. A tuning range of 300 cm⁻¹ is possible due to the broad gain of the active medium.

3. Results

The emission spectra of two laser modules are shown in Fig. 2 and Fig. 3. Both were measured in pulsed mode with 30 ns pulswidth and a repetition frequency of 10 kHz. The first device with a cavity length of 50 µm (Fig. 2) emits around 3.3 µm and features 11 QW with 4 nm thickness. The single emission-mode is tuned over more than 70 nm with a maximum output power of 20 mWp. For the second device in Fig. 3 emitting at 3.9 µm the tuning range is reduced to 60 nm due to a longer cavity length of 85 µm. The QW are 9.5 nm thick with a maximum output power of 90 mWp. Both spectra were recorded at a heat sink temperature of around -20°C.

![Emission Spectra](image)

Due to the vertical emission, the laser beam is of excellent quality. The half opening angle depends on the size of the used aperture, and is in the range of 1.5° to 3°. The FWHM depends on the stability both of the pump laser and the mechanical setup. The best values achieved are < 0.05 cm⁻¹ and limited by the measurement setup.

References

TUESDAY
20 years of SESAM modelocked lasers - a success story

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Abstract

20 years ago the first SESAM modelocked solid-state laser result was published. Since then we have observed rapid progress in ultrafast solid-state lasers enabling many new scientific and industrial applications. I have been actively involved at the frontier of this field for more than 20 years and can provide some more personal insight into how the field evolved. I will start with a brief description of the status 20 years ago, then continue with the invention of KLM, the SESAM, and the frequency comb technique. Towards the end I will give a brief summary of the many different applications that have been enabled by this rapid progress in ultrafast solid-state lasers (such as material processing, frequency metrology, attosecond science and many others) and finally conclude with an outlook into the current research efforts and challenges.
CONTACT LASER-ULTRASONIC EVALUATION

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The basics of Contact Laser-Ultrasonic Evaluation (CLUE), its advantages and prospects are discussed. Examples of CLUE of aerospace industry products are presented both for metal parts and composite structures. The 3-D pictures of internal structure of heterogeneous material provided with CLUE are presented. Possible applications of CLUE in aerospace industry, shipbuilding, nuclear power engineering, structure health monitoring are discussed.

1. Introduction

Contact Laser-Ultrasonic Evaluation (CLUE) is a ultrasonic testing that utilizes laser excitation of a sharp ultrasonic pulse and piezoelectric detection of acoustic transients with high temporal resolution. Optoacoustic (OA) transducer integrates laser excitation and piezoelectric detection of ultrasonic pulses in one unit [1]. This makes it possible to optimize both the efficiency of thermooptical excitation and piezoelectric detection. So, low energy laser pulse produces high amplitude ultrasonic pulse and wide-band detection provides high sensitivity, high temporal resolution and smooth wave front of an ultrasonic beam.

Its schematics is presented in Fig.1. A laser pulse of 10 ns is delivered to the OA transducer with an optical fiber. Laser radiation is focused to the OA-generator, that is placed on the bottom surface of transparent OA prism. At the upper surface of the prism piezoelectric detector is posed. A preamplifier transforms the high output impedance of the detector to low impedance of an electric cable.

![Figure 1. Schematics of an optoacoustic transducer CLUE-P-6 and automated testing system.](image)

In a course of absorption of laser pulse instant heating of OA-generator takes place. Due to thermal expansion of heated layer, the acoustic pulses are launched into the OA-prism and a test object attached to the rear surface of the OA-generator. The rear surface of the OA-generator is the “object” surface of the OA-transducer. Then it operates like convenient ultrasonic testing. Application of CLUE with OA-transducer for non-destructive testing and material evaluation was discussed in details in [2,3].

2. Experimental cases

Metal and composite parts explored in aerospace industry were tested. In each case the 3-D picture of tested sample structure was get point by point in echo regime. The diameter of a probe ultrasonic beam and parameters of digital spectral filter was designed to optimize the contrast of the image. Some examples of the results of testing are presented below.

The nickel crystalline turbine blades were tested in order to visualize the cracks in a stiffening rib (see Fig.2 left). Such defects are fatal for turbine blade and should to be specified. In our case both natural and artificial crack placed in a rib one above another is evidently detected due to diameter of ultrasonic beam (~1 mm) being smaller, then thickness of the rib (2 mm). Short duration of a probe ultrasonic pulse (~50 ns) provides high in-depth resolution at a level of 0.15 mm. Practically it’s impossible to investigate such object with conventional ultrasonic testing.
The results of CLUE of honeycomb structure are presented in Fig.3. The picture shows the profile of the bottom surface of adhesion layer, connecting honeycomb ribs and covering CFRC plate. For regular zone (left) the adhesion forms periodic structure with maximum thickness at the ribs. The scarcity of adhesion appears as irregularities of the profile (right panel) and smaller thickness of the layer.

3. Conclusions
Contact Laser-Ultrasonic Evaluation can be effectively used for non-destructive testing of complicated mechanical parts and structures, particularly in a case of convenient testing failed.

4. Acknowledgments
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References
MECHANISM OF FEMTOSECOND LASER NANO-ABLATION FOR METALS

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Ablation threshold of metals have been investigated experimentally and theoretically since the 1990s with respect to the mechanism of femtosecond laser ablation. Three ablation thresholds have been identified for metals irradiated with a laser pulse of ≤ 400 fs at a wavelength of 800 nm [1]. Two of the thresholds are characterized by the electronic thermal conduction length (l ∼ 80 nm) and optical penetration length (δ ~ 10 nm), respectively. The ablation rates at these thresholds are well expressed by the two-temperature thermal diffusion model. However, the third (low) ablation threshold can not be characterized by this model because the ablation rate is ~0.01 nm/pulse (less than one atomic layer) and the threshold is strongly dependent on laser pulse duration [2]. The ablation rates are well explained by the assumption of multiphoton absorption. We defined this region which characterized by the low ablation threshold as “nano-ablation”. As a results of the nano ablation, high energy singly charged ions are emitted from metal surface and periodic grating structure is self-formed on metal surface.

In this paper, the mechanism of the nano-ablation for metals is reviewed and the current study for discussing the nano-ablation is introduced.

1. Energetic ion emission from metals in femtosecond laser nano-ablation.

In order to elucidate the dynamics of the ejected particles, the velocity distribution of ions emitted from the metal by femtosecond laser ablation has been measured by time-of-flight (TOF) mass spectrometry. However, the observations were limited to a laser intensity of one order of magnitude higher than the low ablation threshold since less than one ion is ejected near the threshold per pulse. Therefore, the velocity distribution could not be obtained by single-pulse laser irradiation. With regard to the laser intensity at the low ablation threshold, the absence of collisional and Coulomb effects or chemical reactions in the ablation plume are expected. Thus, the TOF velocity distribution reflects the surface dynamics of ion ejection. In the experiment, femtosecond laser ablation of Cu by short pulse laser irradiation (800 nm, 130 fs) was studied with TOF mass spectrometry (Jordan D-850) [3] in the laser energy fluence range of 0.028 - 14.4 J/cm². Three thresholds for ion emission were identified as shown in Fig.1. The number of emitted ions per laser pulse Nᵢ was dependent on laser fluence and was in good agreement with Nᵢ ∝ F⁴ for laser fluence of Fₜh,L - Fₜh,M, Nᵢ ∝ F³ for laser fluence of Fₜh,M - Fₜh,H, and Nᵢ ∝ F² for Fₜh,H [4]. The process of ion production is well explained by multi-photon absorption and optical field effects. High-energy Cu ions of 30 eV were produced at a low laser fluence of 0.136 J/cm². The most probable energy of Cu ions increased as the laser energy fluence increased. The experimental results were analyzed within the framework of the Coulomb explosion of ions that were localized to the metal surface, which could satisfactorily and qualitatively explain the obtained results [4][5].

Figure 1: (a) Number of detected Cu ions as a function of laser energy fluence. (b)-(c) Intense laser irradiation can ionize metal instantaneously by the optical field ionization via multiphoton absorption and produce metal ions. Vertical and horizontal axes show the energy level of a free electron and space x, respectively. x=0 shows the interface between the metal and vacuum. The energy level on the vacuum side is distorted by the electric field of the laser perpendicular to the surface. The distortion of the energy level (triangle shape) induces photoelectron ejection via tunneling. γₒ is the Keldysh parameter under the m-photon absorption modified by authors. Under the ion emission thresholds, the tunneling criterion is satisfied as γₒ = 0.013 for three photons, γₒ = 0.47 for two photons, and γₒ = 0.43 for one photon [4].
2. Periodic grating structures formation in femtosecond laser nano-ablation.

Recently, the formation of grating structures on metal surfaces has been observed \[6\]-\[7\] and used in chemical application\[8\]. For fluence levels near the low ablation threshold, the grating structures had an interspace of 300 nm, which was much shorter than the laser wavelength of 800 nm. The interspaces of the grating structures depended on laser fluence, and this phenomenon was well explained by the parametric decay model \[9\] proposed by Sakabe et al. To confirm the validity of this model, the interspaces dependence on laser fluence for Ti, Pt, Mo, and W have been measured experimentally \[10\]. We found that the experimental results agreed reasonable well with this model. In this model, a femtosecond laser pulse interacts with the metal and a photon in the IR region, and a plasma wave decays along the surface. The plasma wave travels slowly at a speed of less than \(10^2\) times that of light, and an ion-enriched local area appears. Before the next electron wave peak arrives, the ions experience a strong Coulomb repulsive force and can be exploded into a vacuum; in other words, a Coulomb explosion \[11\] occurs. Through this process, periodic grating structures are formed. The mechanism of grating structure formation is currently under investigation. In the experiments, \(\lambda=800\) nm, \(\tau=160\) fs, 10 Hz has been used. The laser beam is focused to a spot size of 45 \(\mu m\) on the target surface with a lens \(f=10\) cm, at normal incidence in air. To avoid nonuniformity of intensity in the irradiated area on the surface, the laser intensity distribution is adjusted to be spatially uniform. The targets are Ti and Mo metals, which are mechanically polished. The roughness, \(R_a\), is less than 2 \(nm\) for metals. The fluence is varied in the range of \(F=50-2100\) mJ/cm\(^2\). The number of irradiating pulses is 50. Laser-produced surface structures are examined by scanning electron microscopy (JSM-5560, JEOL). The periodic grating interspace is determined by reading the peak value in the frequency domain after taking the Fourier transform for the 20 \(\mu m\times 15\) \(\mu m\) area of the SEM image, which is equivalent to the laser irradiated area on the targets. The resolution of the present measurements of the periodic spacing is better than 34 nm. Figure 2 shows typical dependence of the periodic structure interspacing on laser fluence, and this phenomenon was well explained by the parametric decay model, in which ablation threshold is taken into account. As shown in Fig. 2, the model is in good agreement with the experimental results in the fluence range in which periodic grating structures are formed. These experimental results indicate that the formation threshold of grating structure is closely related to ablation threshold.

![Figure 2: Laser fluence dependence of the periodic structure interspaces produced by femtosecond laser pulses (pulse duration: 160 fs at 800nm). Solid lines show calculation results based on the parametric decay model \[9\].](image)

References


Laser-based methods of generation, characterization and application of megavoltage ultrashort terahertz pulses are discussed in the present talks. Special attention is paid to the use of THz pulses for visualization of remote objects with high spatial resolution.

In this talk we present the experimental results on generation, characterization and application of megavoltage ultrashort terahertz pulses. Aiming to reach a possibly higher THz electric field amplitude (as high as $10^7$ V/cm) we use the method of generation of THz pulses based on optical rectification of femtosecond laser pulses with tilted pulse front in lithium niobate crystals. We also developed the laser-based terahertz system consisting of a sub-terawatt femtosecond laser (pulsewidth 70 fs, energy 30 mJ, wavelength 912 nm) and a wide-aperture (30x10x10 mm$^3$) MgO:LiNbO$_3$.

As to the use of THz radiation for visualization of remote objects we proposed and realized the experimental technique allowing one to record two- and three dimensional terahertz portraits of spatially nonuniform tested objects with spatial resolution as high as the diffraction limit.

The developed technique and the experimental setup are the base for the next step of the studies aiming at further practical realization of teravision acquisition and processing tools. The developed experimental setups, the results obtained and the prospective applications of high-intensity THz radiation are described and discussed in details.

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Experiments in terahertz optics: A review of new results at Novosibirsk free electron laser

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Novosibirsk free electron laser is a unique source of monochromatic high-power terahertz radiation. These specific features enable experiments which cannot be done on other terahertz sources. In this paper described are recent experiments on the study of diffractive optical elements, holography systems, subwavelength diffraction, Talbot effect, and surface plasmon polariton transmission and decoupling.

1. Introduction

Most terahertz optical experiments, including time-domain imaging and spectroscopy, have been carried out using low-power wide-spectral-band systems. In the terahertz range, there were practically no optical experiments using schemes typical to classic optics in the visible spectral range, because of the lack of appropriate radiation sources, as well as detectors. Monochromatic THz sources of intense terahertz radiation allow realization of such schemes. Novosibirsk terahertz free electron laser [1] and four terahertz sensors of different kinds (see [1 - 4]) were applied to examination of a number of diffractive optical elements (DOE) designed for manipulation of THz radiation, implementation of holography systems adapted to the terahertz range, investigation into THz wave transmission through near- and sub-wavelength slits and hole arrays, and research of surface plasmon polaritons (SPP) traveling along metal-dielectric interfaces. In the last case, SPP decoupling at the tail edge of samples was thoroughly examined both experimentally and theoretically. We carried out experiments on tuning the laser wavelength to 130 or 141 µm. The relative line width was less than 1%.

2. Diffractive optical elements for manipulation of high-power THz radiation

Diffractive optical elements made of very thin plastics or high-resistivity silicon are beneficial to manipulation of high-power monochromatic terahertz beam, which can easily damage conventional spherical plastic lenses. Silicon binary diffractive lenses (BDLs) and silicon beamsplitters (BSs) were designed and produced by TYDEX, J. S. Co, St. Petersburg, Image Processing Systems Institute RAS, Samara, and Samara State Aerospace University, Samara. The BDLs were two-level diffractive lenses with a diameter of 30 mm (f = 120 mm @ λ = 130 µm), the Fresnel zones etched on a high-resistivity silicon plate 1 mm thick. For λ = 141 µm, we observed two focuses at distances of 121 and 42 mm, in good agreement with the theory. The diffraction efficiencies were 17% and 2.4% for the main and secondary focuses, respectively. For the BDL with antireflecting coating, they were 40% and 3.6%. A BS of 30 mm in diameter with a rectangular grating etched on a silicon plate and a TPX lens with a focal length of 50 mm were placed across the laser beam. The image in the focal plane was recorded with a microbolometer focal plane array (MFPA) [3]. The distance between the zero-order and first-order focal points enabled us to measure the diffraction angle of the grating, which turned out to be 15°. The BSs and BDLs have good radiation resistance.

We examined three samples of large-numerical-aperture polypropylene kinoform diffractive lens 0.8 mm thick (KDL) fabricated by Technological Design Institute of Scientific Instrument Engineering SB RAS, Novosibirsk, via hot pressing. For a lens with a diameter of 80 mm and f/D ~ 1, the focal spot diameter was 0.23 mm (FWHM) at a distance of 77.6 mm and a wavelength of 140 µm. The first-order focus, which could be seen in accordance with the theory at 25 mm, was out of the scanning range.

3. Holography

Classic holography in the terahertz region can be implemented thanks to monochromaticity and high power of NovoFEL radiation. Terahertz in-line reference-beam holography has been implemented using a thermal-sensitive luminescence plate [2]. Holograms of amplitude and phase objects were recorded and numerically reconstructed. The spatial resolution of reconstructed images reached 0.4 mm at a wavelength of 0.13 µm. The main obstacle to attaining better spatial resolution is the relatively high transverse thermal conductivity of the plate used. To overcome the problem and, in addition, to realize real-time hologram recording required in some applications, we have studied holography systems with MFPAs. Because of the small physical size of MFPAs (16x12 mm) and tiny pixels (51x51 µm), the arrays can hardly be applied to high THz frequencies (wavelengths λ = 100 ÷ 200 µm) but can be more adequate for radiation of the NovoFEL second stage (wavelengths λ = 40 ÷ 80 µm).
4. Transmission of monochromatic THz radiation through small slits and hole arrays

Transmission of terahertz radiation through small apertures was studied for different metal masks. The Talbot effect on periodic structures with a near-wavelength size of openings was examined in the THz range. The Talbot images had normal appearance for openings of up to $3\lambda/4$ in diameter, and the transmission decreased abruptly for holes with a half-wavelength diameter. Transmission through the slits differed for TM and TE waves. In the latter case, the observed diffraction patterns were clear even for a slit up to $\lambda/4$ wide.

5. Terahertz SPPs: traveling along plane and curved surfaces and decoupling at the sample tail edge

Surface plasmon polaritons were formed using the waveguide technique. Their transmission along gold-air and gold-ZnS-air interfaces was studied. Because of inevitable appearance of bulk wave in such experiments, the intensity of which may exceed substantially the intensity of SPP, it is usually very difficult to obtain real SPP characteristics. To separate the bulk wave and SPP, we used samples of different shape as shown in Fig. 1. In configurations (a) and (b), the Goley cell and the MFPA were used as detectors. The SPP path length was 31 mm for gold surface and 11 mm for gold with a ZnS layer 0.75 mm thick. The surface electromagnetic wave was better coupled to the surface in the latter case.

Using the same sensors, we studied in detail characteristics of terahertz electromagnetic field (EMF) arising when the SPP reaches the tail edge of the sample. This enabled us to study the distribution of intensity over the wave fronts at any distance, directional diagram of the EMF, etc. A rigorous theoretical description for diffraction of a surface wave on a rectangular wedge with impedance faces was performed by I. N. Kotelnikov. The simulations appeared to be in good agreement with the experimental results. The main feature of the decoupled free EMF is its very low divergence. This fact is obviously favorable for THz communication systems and low-range THz radars.

Travelling of SPPs over shaped surfaces (Fig. 1, c) and copper wires was studied using an optical system with MFPA as an imaging device, Goley cell, and cryogenic NbN hot-electron bolometer [4]. These complementary diagnostic techniques enabled us to discover many details which will be described in the talk.

6. Acknowledgements

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References

Terahertz time-domain spectroscopy (THz-TDS) [1] has revealed the extraordinary sensitivity to crystalline order [2], temperature of the sample [3] and the conformational form of the molecule [4]. In molecular crystals the assignment is complicated, for instance, by the presence of both internal and external modes (vibrations within molecules and intermolecular ones). There have been numerous attempts to distinguish the signature of external and internal modes in the THz spectra of various molecular crystals by comparing the spectra of samples with similar crystalline structures, by analyzing temperature dynamics of the spectra or by comparing the experimental data with simulations of an isolated molecule.

In the present paper we aim at studies of the influence of changes of intermolecular bonding in molecular crystals on those of vibrational spectra by means of THz-TDS and Raman spectroscopy on the example of several biological molecular systems. The studied molecular crystals are related to the weakly associated solid-state systems where most intermolecular interactions are dominated by Van der Waals and hydrogen forces. Modeling of these systems with the DFT calculations using standard quantum chemical packages (e.g. Gaussian 03) in general allows one to identify internal vibrational modes of isolates molecules that in some types of molecular crystals permits quality interpretation of low frequency spectra.

We present the review of the recent results on the interaction of terahertz radiation with the complex biological molecular systems and nanostructures. The influence of the radiation on the fictional activity of enzymes is also discussed. A sufficient part of the lecture will be directed to the discussion of the prospect of the THz diagnostics of biopolymers.

We also discuss the study the dielectric properties of nanodispersed materials, such as nanostructured aluminum oxyhydroxides (NOA) and their modification by surface silica (NOAM) in terahertz (THz) frequency range. We discuss the structural sensitive spectra if we change of the material’s annealing temperatures and their chemical composition.

References

While a spectrometer based onto multipliers chains is able to work without laboratory environment, suitable for in situ measurement, frequency above 1.5 THz still requires specific facilities. Two THz spectrometers have been implemented, and their specifications have been assessed by spectroscopic measurements of atmospheric compounds. Fundamental investigations focused onto hydroxyl radicals are proposed by means of THz photomixing spectrometer around 2.5 THz and a versatile electronics based spectrometer is used to analyse unknown industrial samples.

1. Introduction
Despite the THz frequency domain is often denoted as « spectral gap », this region has been actively used for many years for fundamental rotational/vibrational spectroscopy of interstellar chemical compounds started as soon as 1963 with the detection of $\lambda$-doubling transitions of OH radical [1]. Astrophysics community has quietly and successfully utilized THz radiation for a number of decades revealing significant information about interstellar chemistry. Numerous other applications have emerged since 1990 due to the development of the new technique of THz Time Domain Spectroscopy (THz-TDS). Among then, we have noted only few devoted to the detection and quantification of pollutants or atmospheric compounds [2] [3] [4]. Despite the lack of interest for the pollutant monitoring in the THz region, this spectral domain offers many advantages. Strongly polar chemical compounds (such as OH, H$_2$CO, HF, HCN, H$_2$O to cite a few) have intense rotational spectra, and then, should ensure their detection at trace level. The translation of the measured fractional absorption into absolute concentration does not require the use of a calibration gas, provided that the spectral parameters are well known. Moreover, at low pressure, the Doppler linewidth offers a very high degree of selectivity that even a complex mixture should be identified and quantified. At higher pressure, atmospheric absorption, broadening and interferences between different lines from the same compounds and others, make the spectrum difficult to assign. Sensibility and selectivity decrease at ambient pressure, and require longer frequency sweep.

2. High resolution THz spectrometers
2.1 Photomixing spectrometer
Optical heterodyning, also know as photomixing is a flexible solution as a single device is able to cover the entire frequency range from 300 GHz to 3 THz [5]. The experimental photomixing spectrometer setup and the frequency diagram is presented on the Figure 1. A femtosecond frequency comb is presently used to measure and to stabilise the beat note resulting from two external cavity diode laser, and a third diode insures a tunability of 300 MHz. The absolute frequency accuracy of the emitted THz radiation is about 50 kHz and the linewidth is around 100 kHz. Such specifications allow to resolve the hyperfine structure of OH radical recorded around 2.5 THz highlighting the photomixing technique to work at high frequency. We have deduced a OH concentration of \((2.9 \pm 0.7) \times 10^{11} \text{ molecules/cm}^3\) in the plasma produced by an electrode-less radiofrequency discharge in water vapor (Figure 2).

Figure 1: Schematic overview of the photomixing spectrometer and frequency diagram of the tunable synthesiser based on a frequency comb
2.2 Sub THz sources based onto multi-band solids sources.

Commercial solids states elements working at room temperature have been used to implement a versatile sub THz spectrometer. A post-amplified synthesizer drives a cascaded series of frequency multipliers to cover frequency from 100 GHz to 900 GHz via 6 different bands. Output power in the microwatt levels insures room-temperature detection by using different schottky diodes. Versatility of the implemented spectrometer, based on solids sources, allows relaxing required scientific skills and qualifications in order to work without specific laboratory environment. For this demonstration, we are focused our investigations onto SO2, a well known regulated pollutant. The Figure 3 shows an absorption line of a calibrated mixture of 100 ppm of SO2, recorded around 700 GHz by using a frequency modulation technique associated to a detection at the second harmonic. The signal to noise ratio is estimated around 200 for a line intensity of $2 \times 10^{-21}$ cm$^2$/molecule cm$^{-2}$. Demonstrated sensibility has permitted to analyze unknown samples produced during different steps of a process used in a typical metallurgic industry. Future experiments should be devoted to in situ measurements.

![Figure 3](image)

Figure 3: Absorption line of a calibrated mixture of SO$_2$ recorded via one meter of absorption cell. The pressure is 0.1 mb.

3. Conclusions

THz domain is an attractive frequency region being able to provide detailed molecular informations. The “famous THz gap” tends to be filled, thanks to different recent approaches from the state of art of photonic conversions to commercial systems. We are confident that new generation of photomixers should lead toward new THz facilities for fundamental investigations above 1 THz [6]. In situ applications without specific scientific environment will have to benefit from turnkey systems commercially available based onto multipliers chains, but restricted to lower frequencies.

References
PHOTOTHERMAL MODULATION OF A SILICON RING RESONATOR USING THE SEMICONDUCTOR-TO-METAL TRANSITION IN VO₂

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The need to replace switching via metal interconnects by all-optical modulators is driving intense interest in silicon photonic devices, such as ring resonators and Mach-Zehnder interferometers. Here we describe the first demonstration of photothermal modulation of ultracompact, lithographically fabricated hybrid silicon-vanadium dioxide (VO₂) ring resonators, based on the large change in refractive index as the VO₂ undergoes a semiconductor-to-metal transition. Given the ultrafast (∼100 fs) optical switching of the SMT in VO₂, this experiment paves the way in principle to GHz and ultimately THz modulators. However, to reach the THz switching speeds, it will be necessary to find ways to optimize the VO₂ interaction with the resonator to minimize recovery time from the metallic phase.

1. Introduction

Silicon-based optical modulators are emerging as leading candidates for all-optical telecommunications devices and architectures. [1] The micro-ring resonator in particular is a leading platform for high-throughput optical modulators, because of its compact size and adaptability to wavelength-division multiplexing [2]. Silicon micro-ring resonators have achieved ∼GHz speeds by electro-optic modulation [3], as well as all-optical switching and logic operations [4, 5]. However, all-Si optical modulators are limited in speed and performance by relatively weak plasma dispersion, sensitivity to environmental parameters, power-compensation requirements and relatively long carrier lifetimes.

In this paper, we describe photothermal modulation of a hybrid Si-VO₂ optical modulator based on the optically triggerable, reversible semiconductor-metal transition (SMT) in VO₂ as the switching element on an ultra-compact silicon micro-ring resonator. Large changes to resonant wavelength and optical transmission can be achieved by photothermally triggering the SMT, while using only a very small (0.28 µm²) active area of VO₂ on a low mode-volume (∼1 µm³) resonator. This is a first step toward THz modulation of optical signals using similar hybrid Si-VO₂ platforms, capitalizing on demonstrated femtosecond switching in VO₂.

![Figure 1](image1.png)

**Figure 1.** Measured white-light reflectivity of a 60 nm thick film of VO₂ on a silicon substrate, showing the reversible insulator-to-metal transition. Red data indicate the reflectivity during the insulator-to-metal transition, blue data during cooling.

![Figure 2](image2.png)

**Figure 2.** (a) SEM images of a 1.5 µm radius device, (b) a 10 µm radius device, and (c) enlarged image of a sub-micron VO₂ patch on the ring in (b). (d) EDX / SEM mapping revealing elemental distribution of the micro-ring.

![Figure 3](image3.png)

**Figure 3.** Transmission spectra for the 1.5 µm radius hybrid Si-VO₂ ring resonator before and after the SMT was triggered photothermally triggered. The inset shows the geometry of the experiment for the pump laser on.

2. Device fabrication

Devices were fabricated on silicon-on-insulator (SOI) substrates with a 220 nm Si(100) device layer and 1 µm buried oxide layer. Two separate stages of electron-beam lithography (EBL) defined the positions of the silicon rings-waveguides and the VO₂ patches. Following exposure and development of the ZEP 520A resist, the ring-resonator patterns were transferred to the silicon device layer by anisotropic reactive-ion etching. The second EBL stage precisely positioned windows in the resist for localized VO₂ deposition. Amorphous oxygen-deficient VO₁ was deposited within
the selected windows by electron-beam vaporization of V₂O₄ powder (100 mesh, 99.5% purity). Following lift-off with acetone, samples were annealed under 250 mTorr of oxygen at 450°C for five minutes to form polycrystalline VO₂.

During device fabrication, 70 nm-thick films of VO₂ were simultaneously deposited on Si(100) substrates as witness samples, and subsequently characterized by temperature-dependent, white-light reflectivity measurements (Fig. 1). Heating the film beyond a critical temperature, ~63°C, produced a dramatic increase in reflectivity, indicating the onset of the SMT. Subsequent cooling of the device reversed the SMT as the film reverted to the initial semiconducting state. The narrow hysteresis, large contrast, and steep slope indicate the high quality of the VO₂ films. X-ray photoelectron spectroscopy (XPS) measurements on similarly deposited films also confirmed the presence of highly stoichiometric VO₂.

Figure 2 shows SEM images of typical hybrid Si-VO₂ micro-ring devices. Figure 2a shows a typical ultra-compact, low mode-volume, (1 µm³) resonator, with a 560 nm-long patch of VO₂ deposited on a portion of the ring (Fig. 2c). A coupling air-gap of 75nm was used to achieve near critical coupling. Micro-ring devices with different ring radii or VO₂ patch sizes were fabricated (Fig. 2b and d); tuning the ring size or effective VO₂ coverage allowed precise control over the magnitude of the resonance shift induced by the SMT. In addition to SEM imaging, energy-dispersive x-ray spectroscopy was used to map the elemental composition of a model hybrid device, as illustrated in Fig. 2d.

3. Device performance

Figures 3a,b reveal the optical response of the 1.5 µm radius hybrid Si-VO₂ micro-ring resonator before and after illumination by the pump laser. After the pump laser is switched on, the system is allowed to reach thermal equilibrium and stabilize. Transmission measurements reveal a large blueshift (Δλ = 1.26 nm) in resonant wavelength and greater than 10 dB optical modulation at the initial resonance wavelength, λ = 1567.78 nm. The large blue-shift is attributed to the dramatically reduced refractive index of VO₂ in its metallic state. Additional effects related to the silicon ring waveguide itself are observable: (1) the thermo-optic (TO) effect of silicon, Δn/ΔT = +1.86×10⁻⁴/K, and (2) the free carrier-index (FCI) effect. However, these effects are much weaker than the change in optical response induced by VO₂, and in this experiment carry opposite signs. A control experiment on an all-Si micro-ring resonator of the same dimensions showed, in fact, that the TO and FCI effects nearly cancel. Further testing of these devices is in progress, using nanosecond pulsed laser irradiation to induce the phase transition on a shorter time scale.

4. Challenges to THz modulation of the hybrid ring resonator

The insulator-to-metal transition in VO₂ is accompanied by a structural phase transition (SPT), during which the crystal structure of the VO₂ changes from monoclinic to tetragonal. While the SPT is reversible, it is relatively slow; femtosecond measurements suggest recovery times of order hundreds of picoseconds, depending on fluence. Clearly this presents a major obstacle to THz modulation frequencies.

On the other hand, several possible solutions suggest themselves that we are investigating in related experiments. The standard preparation of VO₂ films produces the semiconducting M₁ phase, in which the chains of V ions are paired in a zig-zag arrangement. However, there is a second phase, the so-called M₂, in which the structure is marginally closer to the rutile, metallic phase and thus presumably might lead to faster relaxation time. The M₂ phase can be stabilized by doping or strain. Another possibility is to hold the fluence near or even below threshold, so that the change in the dielectric function is no more than needed to induce switching. Femtosecond studies of THz conductivity show that just above threshold, the metallic phase is almost completely relaxed within 1 ps, suggesting that the structural phase transition is not fully completed for these low fluences [6]. Most recently, measurements of coherent phonon response in VO₂ films shows that the phonon signature of the semiconducting phase remains until a fluence of about 1.5 times threshold, suggesting that this strategy could be workable.

Beyond the question of modulation speed, numerous questions — including the energy cost of switching, the key driving parameter for all-optical switching architectures — remain to be investigated. At the conclusion of the paper, these questions will be summarized as indicators of potential research directions.

References

This paper reviews our recent results on rare-earth-ion-doped integrated lasers. We have concentrated our efforts on crystalline potassium double tungstates and amorphous aluminum oxide. In the former material class we have demonstrated channel waveguide lasers based on Yb$^{3+}$ doping, operating near 1 µm wavelength with slope efficiencies exceeding 70% and output powers up to 418 mW, as well as a record-low quantum defect of 0.7%. When activating with Tm$^{3+}$, we have achieved lasers operating near 2 µm wavelength with a slope efficiency of 70% and 300 mW output power, which are currently tested for trace-gas sensing of NH$_3$ and CO$_2$.

In Al$_2$O$_3$ layers on silicon wafers, when doped with Er$^{3+}$, we have demonstrated a distributed-feedback channel waveguide laser at 1.5 µm wavelength with a free-running line width of 1.7 kHz. Yb$^{3+}$ doping has resulted in distributed-feedback and distributed-Bragg-reflector channel waveguide lasers with 67% slope efficiency and up to 55 mW output power. Dual-wavelength lasers have been demonstrated with this approach and a stable microwave signal at 15 GHz has been generated via heterodyne detection, which has then been used as a simple read-out for intra-laser-cavity optical sensing of nanoparticles in these lasers.

1. Introduction

Recently rare-earth-ion-doped dielectric channel waveguides have proven their ability to generate highly efficient laser output in the fundamental mode, despite their comparatively high propagation losses. Tight confinement and excellent overlap of pump and signal mode, potentially in combination with higher dopant concentrations, as well as high outcoupling degrees, in some cases utilizing only the Fresnel reflections from the two waveguide end-facets, enable laser slope efficiencies approaching the Stokes limit, as well as to obtain record-low quantum defect. Besides, the rigidity of the monolithic channel waveguide geometry allows one to generate ultra-narrow laser line widths without the need for active stabilization. Here we review our recent achievements obtained in crystalline potassium double tungstates and amorphous aluminum oxide.

2. Yb$^{3+}$- and Tm$^{3+}$-doped potassium double tungstate channel waveguide lasers

Rare-earth ions doped into the monoclinic potassium double tungstates KY(WO$_4$)$_2$, KGd(WO$_4$)$_2$, and KLu(WO$_4$)$_2$ exhibit very high absorption and emission cross-sections, making these host materials excellent candidates for solid-state lasers [1]. High-quality monoclinic KY(WO$_4$)$_2$ optical waveguides were grown by liquid-phase epitaxy and laser operation of an Yb$^{3+}$-doped KY(WO$_4$)$_2$ planar waveguide was demonstrated for the first time. Continuous-wave laser emission near 1 µm was achieved with an output power of 290 mW and a slope efficiency above 80% [2]. Co-doping a KY(WO$_4$)$_2$ layer up to the complete replacement of Y$^{3+}$ with suitable fractions of optically inert Gd$^{3+}$ and Lu$^{3+}$ ions, which change the lattice constants in opposite directions, allows for lattice-matched layers with a large increase of the refractive index contrast with respect to the KY(WO$_4$)$_2$ substrate. This paves the way for the realization of integrated optical circuits [3]. Continuous-wave laser operation in a planar waveguide configuration was observed at 1025 nm. A maximum output power of 195 mW and a slope efficiency of 82.3% were obtained, which is the highest value yet reported for a planar waveguide laser to date [4]. In KGd$_{1-x}$Lu$_x$(WO$_4$)$_2$:Yb$^{3+}$ channel waveguides grown onto KY(WO$_4$)$_2$ substrates and microstructured by Ar$^+$ beam etching [5], we produced 418 mW of continuous-wave output power at 1023 nm with a slope efficiency of 71% versus launched pump power at 981 nm [6]. By grating tuning in an extended cavity and pumping at 930 nm, we demonstrated laser operation from 980 nm to 1045 nm. When pumping at 973 nm, lasing at 980 nm with a record-low quantum defect of 0.7% was achieved [6]. Laser experiments were also performed on planar [7] and buried, ridge-type channel waveguides [8] in KY$_{1-y}$Gd$_y$(WO$_4$)$_2$:Tm$^{3+}$. With 8at. % Tm$^{3+}$ concentration, a slope efficiency of 70% and output powers up to 300 mW around 2 µm were obtained, see Fig. 1 (left) [9]. Lasing was obtained at various wavelengths between 1810 nm and 2037 nm. The fabrication of Bragg gratings on top of the channel waveguide will enable temperature-tunable narrow-linewidth operation for trace-gas detection of NH$_3$ and CO$_2$.

3. Er$^{3+}$- and Yb$^{3+}$-doped aluminum oxide channel waveguide lasers

Rare-earth-ion-doped Al$_2$O$_3$ planar waveguides were deposited onto thermally oxidized silicon wafers by reactive co-sputtering [10]. Ridge-type channel waveguides with propagation losses as low as 0.2 dB/cm were microstructured into these layers by reactive ion etching [11]. For optimum Er$^{3+}$ concentrations in the range of 1 to 2×10$^{20}$ cm$^{-3}$, internal net gain was obtained over a wavelength range of 80 nm (1500-1580 nm) and a peak gain of 2.0 dB/cm was measured at 1533 nm [12]. Efficient, ultra-narrow-linewidth channel waveguide lasers in distributed-feedback and distributed-Bragg-reflector configurations [13] were demonstrated in Al$_2$O$_3$:Er$^{3+}$ at 1542 nm [14] and Al$_2$O$_3$:Yb$^{3+}$ at 1022 nm [15].
the former with a linewidth of 1.7 kHz, corresponding to a laser $Q$-factor [16] of $1.14 \times 10^{11}$, and the latter with a slope efficiency of 67% versus launched pump power and output powers up to 55 mW. In a dual-wavelength channel waveguide laser in Al$_2$O$_3$:Yb$^{3+}$ whose operation is based on optical resonances induced by two local phase shifts in the distributed-feedback structure by adiabatic widening of the waveguide, a stable, 9-kHz-linewidth microwave signal at ~15 GHz was created via the heterodyne photo-detection of the two laser wavelengths, see Fig. 1 (right) [17]. We exploited this ultra-narrow line width and its simple read-out via beat-signal generation to perform intra-laser-cavity optical sensing by disturbing one of the two phase-shift regions, resulting in the detection of microspheres with diameters down to 500 nm [18].

Figure 1: (left) Input-output curves of a Tm$^{3+}$-doped potassium double tungstate channel waveguide laser with up to 70% slope efficiency (figure taken from [9]). (right) Stable beat-signal generation from a dual-wavelength Yb$^{3+}$-doped distributed-feedback laser in aluminum oxide (figure taken from [17]).

References


E-BEAM FABRICATED OPTICAL NANOSTRUCTURES

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We have been developing fabrication techniques for optical nanostructures using high end e-beam lithography. The challenging task is the acceleration of the writing process with the aim to enlarge the area respectively number of nanostructures enough for real applications. Based on approaches like double patterning, on edge lithography and pixelated gradient effective media we developed optical elements writeable on areas of dm² within a couple of hours, as follows blazed gratings, diffractive elements, wiregrid polarizers, plasmonic nanorings and metamaterials.

E-Beam Lithography combines high resolution as well as high flexibility. This leads to a type of lithography common for checking new ideas within fundamental research topics like nanotechnology or nanooptics. On the other hand, pattern quality, placement and productivity are critical parameters to be discussed. These parameters are different in several orders of magnitudes, depending on the e-beam system and the fabrication strategy used. We demonstrate our strategies applying e-beam lithography for basic research and real applications with focus on high quality pattern by simultaneously high exposure speed.

The talk starts with the statistics of electron interaction to explain the electron dose for the desired pattern quality needed. This means the resolution limit as well as the edge roughness scale with the minimum electron dose respectively resist sensitivity.

The following section of the talk covers the optimization and parallelization of the writing process by variable shaped beam and cell projection on the e-beam system SB350OS (Vistec). Cell projection (projection of an image of 2.5 µm x 2.5 µm area) is able to speed up the writing up to nearly 3 orders of magnitude.

Finally, by applying approaches like double patterning, on edge lithography and pixelated gradient effective media we reach ultra-fast e-beam writing to allocate nanostructures/nanomaterials for research and industrial applications. Typical elements fabricated are blazed gratings, diffractive elements, wiregrid polarizers, plasmonic nanorings and metamaterials. Typical writing times for the ultra-fast writing are 4-10 hours for a 100 mm x 100 mm area. Some examples can be seen in figures 1-4.

Fig. 1: Diffractive optical elements realized by a pixelated gradient effective media approach fabricated by variable shaped electron beam lithography.
Fig. 2: Iridium wire grid polarizer fabricated by double patterning based on electron beam lithography. The initial grating with 200 nm period was written using cell projection. The writing time was 4 s/mm².

Fig. 3: Aluminum nanorings fabricated by double patterning and variable shaped electron beam lithography. Outer diameters: 90 nm, 130 nm and 190 nm; Minimum feature size: 30 nm; Writing time variable shaped beam: 10 µs per ring, estimated writing time cell projection: 2 s/mm².

Fig. 4: 3D L-particle made of gold exhibiting circular dichroism fabricated by on edge lithography and variable shaped electron beam lithography. Arm length (width) 180nm (70nm), foot radius (width) 200nm (70nm) and thickness of 30nm; Writing time variable shaped beam: 40 µs per 3D L-pattern, estimated writing time cell projection: 4 s/mm².
MOEMS AND MICROOPTICAL COMPONENTS FOR OPTICS AND TIME-FREQUENCY

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The paper deals with the new applications of MOEMS systems (MEMS), and in particular with free-space MOEMS for optics and time-frequency. After a short overview of this very attractive technology, specific technological problems and solutions of integration are discussed. Then the following examples of recent developments based on silicon and glass technologies are presented: chip-scale microscopes and miniature atomic clocks.

1. Introduction

During the last decade, we assisted to an increasing interest in extending the benefits of MOEMS to guided-wave optics, integrated sensors with nano-scale components and sub-wavelength diffractive MEMS [1] with applications enabling imaging, metrology, advanced optical networks, and manipulation techniques at the nano-scale. A variety of different approaches has been demonstrated: mechanically agile scanning probes; high accuracy and sensitivity integrated optical sensing and actuation of MEMS [2-3]; manipulation of MEMS and NEMS with optical tweezers; high throughput near field optical imaging using nanofabricated probes [4], stretchable photonic crystals dynamically altered, waveguide devices modulated through evanescent coupling or by atomic force microscopy tips, waveguide switches with electrostatic actuation, etc… More recently, some applications are emerging in the field of miniaturized microscopes, integrated interferometers and endoscope imaging with cellular resolution [5]. In this paper, we propose a method of integration for different chip-scale microscopes by stacking micromachined optical components in the vertical direction by use of 3-D transmissive scanning, resulting in the assembling of miniature confocal microscopes as well as array-type Mirau micro-interferometers. MOEMS technology offers also the new integration potentials for miniaturized atomic clocks for ultra-precision time keeping.

2. Chip-scale microscopy

Table. 1. Two on-chip microscopes.

<table>
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<th>µ-confocal</th>
<th>µ-Mirau</th>
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<td>Resolution</td>
<td>2 µm, 3D topography</td>
<td>2.5 µm, 2D topography</td>
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<tr>
<td>Applications</td>
<td>Fluorescent Imaging, lab-on-a-chip</td>
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The field of optical instrumentation is dominated by bulky instruments performing individual measuring tasks with micro- and nano- resolution. There is a need for miniature, low cost, highly portable analytical microsystems, demonstrating the equivalent measurement resolution. The heterogeneous integration of nanostructured microoptical components with micro-actuators by using the surface and bulk micromachining techniques allows the development of highly sensitive arrays of MEMS scanning microscopes and interferometers, not only shrinking the size of these instruments but also making them parallel. Here, the objective is to demonstrate the interest of on-chip integration of microsystems for optical instrumentation, aiming the realization of various compact and massively parallel architectures such as the array of MEMS confocal microscopes [6] or array of Mirau interferometers [7] (see Table 1). The added value of this approach, combining the silicon micromachining and microoptics, is to couple the advantages of optical instrumentation with the potential of MEMS. We propose two complementary approaches of heterogeneous integration: (i) 3D multi-wafer technology combining several dies vertically by using various bonding techniques as shown in Fig. 1; and (ii) micro-assembling with the use of reconfigurable silicon free-space micro-optical bench [8] as shown in Fig. 2.

3. Chip-scale atomic clocks

The combination of CPT physics and MOEMS technologies allows the development of highly miniaturized chip scale atomic clocks (CSACs) [15], obtained in an extremely compact vapour micro-cell of a few mm³, exhibiting a power consumption of about 150 mW and a fractional frequency stability better than 10⁻¹¹ at 1 hour [9].
Fig. 1: 5x5 array of microlenses (2.5 mm) of Mirau interferometer obtained by thermal glass reflow.

Fig. 2: Silicon Free-space reconfigurable microoptical bench.

Such frequency references, outperforming crystal quartz oscillators over long time scales, are intended to provide excellent base timing for numerous portable applications such as telecommunication networks synchronization, navigation or military systems. The heart of a miniature atomic clock consists of a hermetically sealed microfabricated cell containing alkali vapor and a buffer gas atmosphere, formed by sandwiching a silicon wafer with a through-hole between two glass plates and joining silicon and glass plates by means of anodic bonding, thus forming a sealed cavity [10]. The main difficulty of fabrication of such micro-cell is the operation to fulfil it with alkali vapours and introducing the buffer gases, preserving the compatibility with most of the subsequent steps of the cell fabrication. Here, the cesium (Cs) vapor is generated only after complete sealing of the cell by local heating of a Cs metallic dispenser with a laser source [11]. The microcell is made in a wafer of silicon with glass wafers bonded to both sides, containing two cavities: the dispensing cavity in which the metallic Cs dispenser is placed and the measuring cavity where the laser beam generating the CPT signal is collimated (see Fig. 3). The cavities are etched by deep reactive-ion etching (DRIE), as shown in Fig. 4 while Fig. 5 shows a view of a micromachined cell [12].

4. Conclusion

This work matches the definition of new generation of smart systems by creating a platform for developing new concepts of miniature instruments, presenting a multi-disciplinary approach with photonics, microoptics and micromechanics as well as the multi-functionality (in case of microscopes). Our goal is to demonstrate a real potential for the conversion from smart systems to viable products by association of photonics and micromechanical devices, reliable and adapted for fabrication of parallel nano-instrumentation devices, improving the cost-efficiency, performance and functionality of micro and nano-systems, increasing the level of integration and miniaturization and presenting a high degree of innovation and technological novelty.

Acknowledgments

The work was supported by the European STREP project MAC-TFC (grant 224132) and STREP project SMARTIEHS (grant 223935).

References

In a short introduction the principles of Optical Coherence Tomography (OCT) are highlighted and some advantages and limitations of Swept Source OCT (SS-OCT) and Spectral Domain OCT (SD-OCT) are discussed. Two current research projects at the OptoLab of Bern University of Applied Science (BUAS) are presented. The first project concerns the development of a SS-OCT system based on a novel miniaturized swept laser from EXALOS. The second project is an implementation of a custom made SD-OCT in a surgical femto-second laser system from ZIEMR Ophthalmic in order to plan and analyze cornea incision. Both OCT realizations suffer under the system inherent mirror ambiguity. Two different approaches to resolve the problem are presented.

1. Introduction

Basically, a frequency domain OCT Systems can be understood as many (mostly 1024 or 2048) spectrally shifted Michelson interferometers in parallel. In the case of Spectral Domain OCT (SD-OCT) the parallelization is obtained by a grating spectrometer and in the case of swept source (SS-OCT) by the time encoded data acquisition. The raw data in both systems are available as a sampled sequence with each element attributable to a spectral bin. The transformation of these frequency domain data points to the spatial domain reflectivity profile is essentially realized by Fourier Transformation. Because the spectral bins are not distributed uniformly in k-space (frequency space), non uniform fast Fourier Transform NUFFT algorithms are used in modern OCT systems.

1.1 Resolution, Fall off and Mirror Ambiguity

The depth resolution of OCT Systems is, as opposed to confocal microscopy, independent of the numerical aperture of the delivery optics. The point spread function of the optical system is entirely defined by the spectral shape of the laser source. Deeper insight into this topic and methods to improve axial resolution are discussed in another presentation. Due to the finite sampling number prior to Fourier Transform, the PSF amplitude will decrease with higher optical path differences (OPD) in the interferometer. (Fig. 1) The maximum detectable frequency, (or OPD) is limited by Shannon’s sampling theorem, the so called fall-off of the signal to noise ratio is represented in Fig 2. Beside this system’s inherent limitation of the measuring range, OCT signals are symmetric respective to zero OPD. This mirror ambiguity is a drawback because only the half measuring range is usable [1].

2. Full range OCT principles

Most of the different methods to unfold the mirror ambiguity are based on acquiring different phase shifted signals in order to produce a complex input signal for the Fourier Transform. This can be achieved, for example, by taking two A-scans at two λ/4 shifted reference arm positions. Because in medical applications acquisition speed of several 10’000 A-scans per second are required, only solutions with parallel registration of phase shifted signals are of interest. A possibility is to exploit the fact that 3x3 fiber couplers induce a 120° phase shift between the three outputs [2]. Another possibility is to encode the phase information in the polarization [3]. A second group of full range methods exploit the non-symmetric behavior of dispersion mismatch in the interferometer. This method is entirely based on signal processing and needs no complicated optical setup, however, this method is demanding in respect to computational costs.
3. Projects

In the first project, we developed a detection unit containing four detectors and two interferometers. The relative phase shifts between the different paths are introduced by retarder plates. The custom designed high bandwidth amplifiers are integrated in the miniaturized unit and the delicate alignment of the free beam optics is achieved by active alignment and glueing of the elements.

The aim of the second project is the fusion of two technologies into one system: Refractive cornea surgery by a femtosecond laser (fs-laser) and OCT 3D imaging. The fs-laser beam is delivered by means of an articulated mirror arm to the handpiece containing the focusing lens on an xy scanner. Prior to the cutting process, the eye is attached to the laser exit window by a vacuum system. A predefined pattern is then cut by the fs-laser.

The OCT laser is coupled into the same path and uses the same focusing optics. A careful optical design enables both, diffraction limited focusing properties of the fs-laser beam and small numerical aperture for the OCT laser beam. A custom spectrometer based frequency domain OCT System was developed and integrated in the fs-laser base station housing. The choice of SLED source and the design of the spectrometer enable an optimal adaption of the resolution and measuring depth. In order to measure the whole anterior segment of the eye, including the crystalline lens, a full-range detection is indispensable. For this purpose dispersion encoded full range DEFR method [4] will be investigated.

References

Optical Coherence Elastography (OCE) is an emerging tool that allows noninvasive assessment of tissue biomechanical properties with high lateral and axial resolution. In this report we demonstrate the capability of OCE to assess surface mechanical wave propagation in phantoms and ocular tissues both ex vivo and in vivo using a Phase Stabilized Swept Source Optical Coherence Elastography (PhS-SSOCE) system. Low-amplitude (<10µm) mechanical waves were introduced by focused air puff excitation on anterior corneal surface of rabbits and mice eyes. The mechanical stimulus propagated through the cornea producing vibrations on the anterior and posterior surfaces of the cornea. The wave amplitudes and velocities were measured at spatially distributed points across the cornea surfaces using a phase-resolved method. The results demonstrate that this method allows measuring ultra-small changes in the wave amplitude (as small as 10 nm). By measuring the wave velocity at these points, a 3-D stiffness map of the cornea in vivo can be constructed which is a subject of our future work.

1. Instructions
   The biomechanical characteristics of ocular tissues can have a profound influence on the health, structural integrity, and normal function of the eye. Keratoconus is one of the most familiar examples of ocular disease influenced by tissue biomechanics. Keratoconus and other similar ectatic diseases of the cornea can cause severe visual disability that predominantly affects young adults in their most productive years of life. Keratoconus (prevalence 1:2000) is one of the leading causes of corneal transplant in the United States and in the developed world.[1-3] Advanced keratoconus is characterized by thinning of the corneal stroma and conical deformation of the tissue causing pronounced optical distortions and poor vision. Typically this condition is diagnosed and monitored using corneal topography to observe and quantify the gross morphological distortion of the cornea, e.g. detecting patients who are unsuitable for corneal refractive surgery. Histological structural changes in keratoconus include disruption of the anterior limiting lamina and disorganization of the anterior stromal lamellae. This provides a theoretical basis for detection of structural alterations that occur before gross morphological distortions are clinically detectable. Therefore, it is critically important to understand the interplay between the mechanical properties of the cornea and its physiological function. More importantly, success of this proposal will easily translate to other applications and advances in related fields of medicine.

   Optical coherence tomography (OCT) is a non-invasive optical imaging modality that allows high speed and high resolution 3-D imaging of tissue structures at a depth of ~ 2-3 mm. Since its introduction in 1991, OCT elastography has been first demonstrated by Schmitt in 1998 [4], where microscopic deformation due to compressive stress has been studied. Since then OCT has been further developed and applied to track tissue displacements by incorporating various optical techniques such as speckle tracking [5, 6], correlation [7-9], Doppler and phase methods [8-10]. However, application of compressive stress is not feasible to the eye, thus limiting their application in vivo. In order to utilize OCT elastography in ophthalmology where relatively low amplitude of mechanical excitation is required, an approach capable of measurements with of high sensitivity is required. Previously, we have demonstrated the application of phase stabilized swept source optical coherence tomography (PhS-SSOCT) in measuring nanometer level amplitudes in murine eye lens [11, 12]. In this paper, we utilize the PhS-SSOCT to demonstrate the possibility of measuring propagation of mechanical waves in tissue-mimicking phantoms and real tissues.

2. Experimental Setup
   The elastic waves on the sample’s surface were generated by either tapping or via focused air puff. The wave propagation was measured using a phase stabilized swept source OCT system (PhS-SSOCT). The details of PhS-SSOCT are described elsewhere.
Briefly, the system was capable of a depth resolution of ~ 8 µm, imaging depth of 4.5 mm, phase stability of 0.04 rad and time resolution of 33 µs.

3. Results and Conclusions

Our preliminary validation studies on measurements of vibrations that were induced on the surface of a speaker diaphragm, gelatin phantom, mouse crystalline eye lens and cornea in vitro with the developed phase-sensitive method. Fig 2 shows typical delay of wave phase response recorded at different locations away from the source. The velocity of the propagating surface shear waves in such phantoms is shown in Fig 3a. The values shown represent the velocities averaged over a 3 mm range. Clearly, shear wave velocity increases with the increase in gelatin concentrations (stiffness). These results were validated by direct stress-strain measurements using In-Spec 2200 portable system as shown in Fig 3b.

Thus, these results demonstrate that the PhS-SSOCT elasticity imaging method is capable of quantifying shear wave velocity and, therefore, shear or Young’s modulus of the tissue.

References


Fig 2: Phase responses recorded at various points away from the source of excitation in a gelatin phantom.

Fig 3: (a) Shear wave group velocities measured at the surface of the 8%-16% gelatin phantoms; (b) Young’s modulus vs gelatin concentration obtained using uniaxial tests. N= 3.[14]
IMAGING AND ANALYSIS OF DEVELOPMENTAL ABNORMALITIES IN MOUSE EMBRYOS USING OCT

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Mouse models of human diseases provide a powerful resource for exploration of molecular regulation of development and pre-clinical studies. A live high-resolution imaging method for mouse embryos would contribute to high-throughput morphological screening of mouse mutants with developmental abnormalities. Recently we have developed methods for live mouse embryonic imaging in static culture at early gestation (E7.5 - E10.5) as well as in utero imaging at later gestation (E12.5 – E18.5) with Optical Coherence Tomography (OCT). In this work we assessed the capability of these recently developed approaches for imaging and analysis of mouse mutant embryos with developmental defects of different organ systems. These results demonstrate that OCT in utero imaging is a potentially useful tool to study embryonic abnormalities in mouse models.

1. Introduction

Every year, about 6% of infants worldwide are born with serious birth defects. Moreover, birth defects are the leading cause of infant deaths. There are thousands of different birth defects, affecting the structure or function of every part of the human body. Despite of the major effort in the biomedical community to understand the nature of congenital defects, 70% of the causes of birth defects remain unknown.

The mouse is a classic mammalian model used to study the anatomical and physiological development of different organ systems due to their small size, fast regeneration, and variability of mouse mutants of human disease available from large scale genetic screens [1]. Previously, we have developed a set of protocols for live mouse embryonic imaging with Optical Coherence Tomography (OCT). Early stage embryos (E7.5-E10.5) can be cultured on the imaging stage for live visualization of cardiodynamics and hemodynamics [2,3] Later stage embryos can be imaged through the uterine wall, which allows repetitive structural analysis of different organs in the same embryos [4]. Here we demonstrate the capability of OCT to perform 3D imaging of different embryonic organs in mouse mutants with developmental defects affecting different organ systems.

2. Materials and methods

2.1 Swept-Source OCT:
The SS-OCT system uses a broadband swept-source laser (Santec) with output power P = 20 mW at central wavelength \( \lambda_0 = 1325 \text{ nm} \) (spectral width \( \Delta \lambda = 100 \text{ nm} \)) and sweeping speed of 30 kHz. The light from the swept-source laser source is divided into a reference arm and a sample arm 10% and 90%, respectively. A balanced-receiver configuration detector (Thorlabs, PDB140C) receives an interferogram formed by the interference of the back reflected light from sample and reference arm. It is then digitized using a 14-bit ADC. FFT reconstructs an OCT intensity in-depth profile (A-scan) from a single scan over the operating wavelength range. Scanning along X and Y direction provides 2D and 3D data collection capabilities.

2.2 OCT Imaging in embryo culture:
Male and female mice were mated overnight. Females were examined for vaginal plugs daily and the presence of a plug was taken as E0.5. Embryos were dissected with the yolk sac intact at E8.5 and E9.5 in the pre-heated to 37°C dissecting medium. The dissecting medium consisted of 89% DMEM/F12, 10% FBS, and 1% 100X Pen-strep solution (Invitrogen, Grand Island, NY). The dissection and imaging stations were heated and maintained at 37°C. The protocols are described in more details in [2,3].

2.3 In utero embryonic imaging with OCT:
For repetitive imaging of developing embryos, the pregnant females at E13.5-E18.5 were anesthetized with isoflurane by inhalation. The mouse was placed on a heated platform to maintain the body temperature at 37°C during the whole
procedure. To optimize visualization of each embryo and accurately identify individual embryos, the gravid uterine horn was externalized through a 1-2 cm incision made in the lower abdomen. The uterus was covered with transparent plastic wrap, which was wiped with ethanol prior to the procedure. After the imaging, the incision was closed using surgical sutures. To minimize post-operative discomfort, Carprofen (5 mg/kg) was administered to the females every 24 hours. More information about the procedure can be found in [4].

3. Results and discussion
To assess the capability of the recently developed imaging approaches for phenotypic embryonic analysis, we imaged a number of mouse mutant lines with congenital defects affecting different organ systems. OCT cardiodynamic analysis was performed in Mlc2a transgenic mouse model in embryo culture. Mlc2a embryos exhibit defect in atrial contraction, which affects blood circulation and results in lack of vascular remodeling. OCT imaging was useful in dynamic visualization of this defect. We also used OCT to visualize eye morphology in a Pax6-SV40 T-antigen transgenic mouse line, which spontaneously forms lens and retinal tumors during embryonic development. We demonstrate that in utero OCT imaging permits us to clearly differentiate between the wild type and the mutant embryos, suggesting that it can be useful for phenotypic analysis of mouse embryos with ocular defects.

The mouse mutant model Pcgf3 is known to exhibit defects in patterning of the bones. Some of the mutants exhibit hindlimb oligodactyly (fewer number of digits) as well. Since this model has high degree of variability of the phenotypes, the time line of the phenotype progression cannot be deducted from analysis of excised embryos at different stages, and the course of the defect development is not understood. Our data indicate that OCT in utero imaging approach is useful for differentiation of the phenotypes with limb abnormalities (Fig 1). Potentially it can be used to track the progression of the disease. These observations suggest that OCT is a promising technique to study different organs in normal and mutant embryos. Implementation of these methodologies in the embryonic research can lead to better understanding of congenital defects.

References

Figure 1. 3D reconstructions of the normal (A) and the mutant (B) embryos. The morphological structure of the hindlimb in the normal embryo (C) is clearly different from the one of the mutant (D).
PHOTONIC-FORCE MICROSCOPY BASED ON OPTICAL TWEEZERS FOR BIOPHYSICAL APPLICATIONS

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Photonic-force microscopy approach based on laser trapping by optical tweezers is discussed. Two examples of application of photonic-force microscopy are presented. First, femtonewton interaction between magnetic Brownian particles prospective for biophysical applications is probed by optical tweezers. A new method of detection of the interaction between magnetic particles by using correlation function analysis of trapped particles motion in liquid based on simultaneous registration of nanometer displacements of the two optically trapped particles in a uniform external magnetic field is developed. Then, a novel approach to probe viscoelastic properties of biocells based on double trap optical tweezers is discussed. Frequency dependence of the tangent of phase difference in the movement of the opposite erythrocyte edges while one of the edges is forced to oscillate by optical tweezers appeared to be highly dependent on the rigidity of the cellular membrane. This allows determination of effective viscoelastic parameters characterizing red blood cells with different stiffnesses (normal and glutaraldehyde-fixed) which can be used for monitoring of red blood cells lifecycle.

1. Introduction

Magnetic particles have a variety of applications in biology, medicine and in the industry of magnetic devices. Research of the properties and applications of magnetic fluids consisting of well-dispersed magnetic particles is rapidly growing. Magnetic forces between microparticles in liquid media are very small being in order of hundreds of femtonewton, so the ability to measure and control the forces is of considerable interest. Brownian motion of single microparticles in solution prevents the direct detection and measurements of the magnetic pair interaction forces. However, these weak forces change statistical properties of microparticles Brownian motion. This allows one to suggest a new method to detect the interaction between magnetic particles by using correlation function analysis of particles motion in liquid combined with the optical tweezers technique [1]. Another group of problems relates to development of various techniques for local viscoelastic properties and deformability of complex materials research ranging from investigation of complex fluids to soft solids. In particular, viscoelastic characterization of cellular membranes is a crucial problem in understanding of tissue physiology. Methods probing the membrane viscoelastic properties provide tools to characterize the physiological state of the membrane and its changes caused by various diseases or drug effects. The most mainstay techniques which allow working with single cells are optical tweezers, micropipette aspiration technique, and atomic force microscopy. Here we report on a new way to employ optical tweezers to dynamically probe viscoelastic properties of the cells. We use so-called active rheology meaning that the motion of the studied objects is analyzed on the frequencies of external perturbations caused by optical traps [2,3]. This approach is the further development of passive rheology monitoring the thermal fluctuations to measure the effect of hydrodynamic coupling on the dynamics of two colloidal particles held in fixed optical traps. A new dynamic parameter, namely, the tangent of phase difference in the movement of the erythrocyte edges, is introduced as an effective finger-print characterizing the state of the cell.

2. Results and Discussion

Photonic-force microscopy is realized by dual beam optical tweezers setup arranged by using two singlemode diode infrared lasers (Lumics LU0975M330, Germany) with wavelength of 980 nm, output power of up to 330 mW. The diode lasers were pigtailed by polarization-maintaining optical fiber and output radiation was collimated by aspheric lenses. The position of one of the optical traps was controlled by acousto-optical deflector -- (Isomet LS55-NIR, USA). An oil immersion objective (Olympus UPLFLN 100XOI2, Japan) with numerical aperture of 1.3, working distance of 0.2 mm and about 60% optical transmittance at 980 nm was used for focusing the laser beams to form the traps. Both laser beams were expanded to the full objective aperture to create maximal optical field gradient in the focal points for the most efficient RBC trapping. Two extra diode laser beams with wavelengths of 635 nm and 670 nm, respectively, and with the output power of 0.3 mW were used to detect displacements of the trapped cell. The latter beams passed through the optical elements controlling the positions and the width of the beams and then were focused into the sample chamber. The forward scattered light was collected by a 40X objective and detected using two quadrant photodiodes (QPDs) (Thorlabs PDQ80A, USA). Displacements of the trapped cell were extracted from the changes in the QPD photocurrent collected by analog-to-digital-converter (National Instruments PCIe-6353, USA) working at the rate of 10^5 samples per second per each channel. CCD camera was used for visual control of the trapped objects. This method is particularly sensitive for measuring displacements of the trapped spherical objects at the nanometer scale. However, the scattering pattern from the nonspherical trapped object, for example from the cell, is complex that restricts the direct measurement of displacements in the trap. Another way to quantitatively analyze the movement of the trapped cell is to measure the relative phase of the cell movement.
In case of magnetic particles, water suspension of silica beads with the size of 400 nm doped by iron oxide (III) fine nanoparticles is used. Experimental results show that magnetic interaction between two colloidal particles considerably changes cross-correlation function of particles Brownian motion. This interaction is able to be extracted from the shape of cross-correlation functions of particles displacement from the equilibrium trap positions upon Brownian motion. Theoretical model of magnetic particles Brownian motion is suggested providing a good agreement with experimental results. Numerical Monte-Carlo simulation was made to determine the applicability limits of the theoretical model and experimental techniques. In case of red blood cells (RBC’s) since the erythrocyte has a relatively large size (about 8 microns) in comparison with the waist size of each trap (~2 microns), optical trapping does not occur in the cell center, but at its edges, where the strongest contrast in the refractive index compared with the environment is. In each experiment single red blood cell is trapped simultaneously by the two traps at the opposite edges with the distance between the traps about 5.9 ±0.1 microns. This distance value makes it possible to work with red blood cells which are not deformed by optical traps. One RBC edge was oscillated with the specified frequency and amplitude using acousto-optic deflector. Laser radiation scattered on the edges of the erythrocyte was used to measure the positions of the RBCs edges using QFD. This allowed us to measure the phase delay in the movement of the erythrocyte edge in the fixed trap relative to the edge trapped by an oscillating trap. Tangent of the phase difference obtained while the cell is doubly trapped by the fixed optical trap and the trap oscillating at the specified frequency in the range from 50 Hz to 1 kHz appears to be an effective measure of the RBC viscoelastic properties. Phase difference tangent is found to be a reproducible linear function of the trap frequency oscillation that allows us to introduce a new effective parameter -- response time -- characterizing the average viscoelastic properties of an individual cell.

References
HIGHLY EFFICIENT SOURCES OF THZ RADIATION: INVESTIGATION AND DEVELOPMENT

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Abstract

Experimental realization of the efficient optical rectification of femtosecond laser pulses in LiNbO₃ crystal in sandwich structure and in the scheme with tilted front altogether with THz generation by two-color laser interaction in a laser induced plasma in ambient air will be considered. The results of investigation of plasma density decay in a plasma filament by THz radiation scattering will be presented as well.

The development of the sources of terahertz (THz) radiation “pumped” by intense femtosecond laser pulses occurs very rapidly at present time. In this talk I revue our results on the investigation of two different schemes based on optical rectification of femtosecond laser pulses in LiNbO₃ (LN) crystal and two-color laser interaction with laser induced plasma in ambient air. The application of the THz radiation for plasma diagnostics is presented as well.

A lithium niobate is one of the promising crystal for THz generation. This crystal has high nonlinear coefficient and wide bandgap that allows using a high power optical pump. However this crystal suffers from high THz absorption and strong velocity mismatch between optical pump and THz radiation. To overcome velocity mismatch it was proposed to use special laser pulses with a tilted intensity front [1]. Tilting intensity front of the optical pulse with respect to the phase fronts results in a phase matching between optical pump and terahertz wave propagating in the direction normal to the intensity front. By using amplified Ti:sapphire laser systems for pumping Mg-doped stoichiometric LiNbO₃, this technique has recently resulted in generation of near-single-cycle terahertz pulses with energies up to 50 µJ [2] and a high conversion efficiency ~ 0.1% [3]. For lower laser pump energy it was demonstrated that cooling of the LN crystal resulted in efficiency increasing up to 4 times [4]. In this talk I present results of THz generation in cryogenically cooled LN at high pump energy for different laser pulse duration and crystal length. Weakly and strongly nonlinear regimes of THz generation were observed in experiment. At weakly nonlinear regime efficiency linearly grew with the optical energy. Maximum slope rate of dependency was obtained for crystal length of 1 cm and pulse duration of 190 fs at T=77°K. For shorter pulse duration (120 fs) the efficiency was 1.5 times lower. At strongly nonlinear regime efficiency saturates and even decreases. Maximum conversion efficiency of ~0.2% was obtained for 5 mm crystal length and 190 fs pulse duration.

Another method for efficient THz generation in LiNbO₃ is based on the Cherenkov radiation mechanism. Non-colinearity of the Cherenkov radiation and the pump laser pulse allows for overcoming of high terahertz absorption in the crystal by organizing the output of the generated radiation through a lateral material with low THz losses, for example silicon [5]. Strong pump focusing needed for implementing the Cherenkov mechanism permits to use low pump energy for efficient optical-to-terahertz conversion. At the same time, line-focusing of the laser pump may be used to scale-up THz energy and generate a Cherenkov wedge with a flat phase front that is more convenient for practical applications than the Cherenkov cone in the spot-focusing scheme. Experimental investigation of Cherenkov terahertz generation in a sandwich structure consisting of a 50 µm (or 30 µm) LN layer, a BK7 substrate and a Si output prism demonstrated 0.1 % energy conversion efficiency for a moderate pump energy of 30-100 µJ [6]. But in that experiment part of the THz energy was lost in the BK7 substrate. Recently a sandwich structure with a totally reflecting surface (metal substrate with a variable air gap between LN and metal) was proposed to collect THz emission in one direction and control the generated spectrum by changing the air gap [7]. In this talk I present experimental investigation of such sandwich structure for pump wavelengths of 800 and 1380 nm. The THz spectrum generated in the sandwich structure (inset in Fig. 1(a)) spreads up to 3.5 THz with a dip near 1.5 THz and has two peaks near 0.8 THz and 2.2 THz. The THz energy is redistributed between these peaks and the dip is shifted by varying the air gap from 0 to 20 µm. For low pump energy efficiency of the optical-to-terahertz conversion linearly grows with pump energy by 1.5 times higher slope for 800 nm pump compare to 1380 nm. For high pump energy efficiency saturates near ~0.25% for 0.8 µm pump wavelength (at pump energy of 20 µJ) and ~0.3% for 1.38 µm pump wavelength (at pump energy of 50 µJ).

Another perspective scheme of terahertz generation is based on using two-color femtosecond laser pulses ionization in ambient air. The terahertz wave generation mechanism was originally attributed to four-wave rectification process through the third-order optical nonlinearity of air. However, it has been suggested that the plasma formation plays an important role in the terahertz wave generation process [8]. In this talk, we report the results of the terahertz wave generation in air using inverted two-color excitation scheme. We used weak fundamental laser pulses (at 1600 nm) and the third-order optical nonlinearity of air. However, it has been suggested that the plasma formation plays an important role in the terahertz wave generation process [8]. In this talk, we report the results of the terahertz wave generation in air using inverted two-color excitation scheme. We used weak fundamental laser pulses (at 1600 nm) and
intense second-harmonic pulses (at 800 nm) to generate terahertz radiation. Fig. 1(b) shows dependence of terahertz pulse energy on the angle between the polarization of fundamental and second-harmonic field. For the case of parallel polarizations of two-color excitation terahertz emission has optimal conversion efficiency and its polarization is the same as the laser pulses has. For the case of orthogonal polarizations of the laser pulses terahertz waves with orthogonal polarization possesses higher power than in parallel polarization. This behavior is in good accordance with plasma current calculations.

The filamentation of intense femtosecond laser beams in air has attracted wide interest during the last decades. We used the generated THz pulses to diagnose the plasma concentration in a filament and its decay. Although several methods were used to measure these characteristics of the filament, including time-resolved diffractometry, longitudinal interferometry, and plasma channel conductivity, our new original method based on transverse scattering of probe terahertz pulses allows to investigate precisely the plasma density decrease within two orders of magnitude. The plasma decay in external electric field was also investigated. To measure plasma density in the filament the terahertz pulses were focused perpendicularly on the plasma filament by an off-axial parabola ($F = 5$ cm). The terahertz radiation scattered by the plasma was collected by a teflon lens ($F = 4$ cm, $D = 4$ cm) into the input of a liquid-He-cooled InSb hot electron bolometer (QMS Instruments). High voltage was applied between the electrodes to introduce external electric field $E_0$ in the region of the plasma filament. Plasma density was found from the experimentally measured scattered THz signal following [9]. It is seen (Fig. 1(c)) that, in the absence of external electric field, plasma density rapidly decreases by about two orders of magnitude (down to $10^{15}$ cm$^{-3}$) in 2 ns. Application of external electric field $E_0$ slows down plasma decay to some extent. To explain the observed fast decay we considered a set of kinetic processes for electrons and ions, including dissociative and three-body recombination, as well as recombination with participation of complex $\text{O}_4^+$ and $\text{N}_2\text{O}_2^+$ ions formed in transient plasma after the ionizing pulse. The dynamics of electron temperature determined by electron, vibration and rotation excitations in the applied electric field was taken into account in the rate coefficients. A good agreement between the experimental results and the theoretical calculation is observed.

Figure 1: (a) Optical-to-terahertz conversion efficiency as a function of the pump energy in the sandwich structure: for 0.8 $\mu$m (crosses) and 1.38 $\mu$m (diamonds) pump wavelength, in the inset THz field spectra at 0.8 $\mu$m; (b) The dependences of terahertz pulse energy on laser pulses polarization. (c) Plasma density decay. Experiment: triangles and circles ($E_0 = 0$ kV/cm), crosses ($E_0 = 4.5$ kV/cm), diamonds ($E_0 = 9$ kV/cm). Theory: solid line ($E_0 = 0$ kV/cm), dashed line ($E_0 = 4.5$ kV/cm), dot-dashed line ($E_0 = 9$ kV/cm).

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Specific features of radiation structure of terahertz quantum cascade lasers are determined by wire geometry of their waveguides with small and subwavelength transverse dimensions and the length much larger than the wavelength. Here we present an overview of the results of beam profile investigations and of the methods proposed for the control of radiation structure of such lasers.

1. Introduction
Terahertz Quantum Cascade Lasers (THz QCL-s) are unipolar devices operating on intersubband transitions in semiconductor heterostructures. The ability to engineer the frequency of lasing transition (presently from 4.8 THz to 1.2 THz), high output power (more than 100 mW at cryogenic temperatures), narrow linewidth (tens of kHz for single mode devices) together with compactness and ease of high speed modulation make the THz QCL-s promising sources for a wide range of applications. However, a number of important applications of THz QCL-s, including using such lasers as a local oscillator for heterodyne spectroscopy, have been hindered until recently due to specific features of their radiation structure. Peculiarities of THz QCL-s radiation pattern stems from their wire geometry: transverse dimensions smaller or comparable to the wavelength, while their length is much larger than the wavelength. Standard methods of laser optics are targeted at the lasers with transverse dimensions much larger than the wavelength. One can expect that the methods of microwave antenna theory dealing with subwavelength sources can be used to control the radiation features of wire lasers. However laser physics sets up specific tasks that have not been addressed by physics of microwave devices: to combine high directivity with high mode confinement, to provide the possibility of frequency tuning, to control and optimize the level of radiative losses providing maximum laser output power. Here we present an overview of the methods developed for the control of the radiation structure of THz QCL-s. It should be mentioned that Thz QCL is a convenient model system for investigation of the properties of wire lasers in general, and the approaches developed can further be applied to lasers of similar waveguide geometry operating in other frequency ranges and based on different active media.

2. Waveguide geometry
Wire geometry of THz QCL-s lasers is determined by practical requirements: limitation of the structural growth times, the need of single mode operation, effective cooling, and minimization of reflection losses. There are two main types of the waveguides that have been used for THz QCL-s: the semi-insulating surface-plasmon, and the metal–metal waveguide. They consist of an active semiconductor structure about 10-μm-thick between two contact layers placed on a dielectric substrate. Both contact layers of metal–metal waveguides are metallic, while one of the contact layers of the surface-plasmon waveguide is formed by a thin heavily doped layer underneath the active region, on top of a semi-insulating substrate. Considerable penetration of the modes of surface-plasmon waveguides into the substrate leads to a smaller mode confinement $\Gamma = 0.1$–$0.5$, that is reduced additionally in the ridges narrower than 100 μm, higher mirror losses, and non-uniform radiation intensity along the waveguide. Metal-metal waveguides allow high mode confinement $\Gamma \approx 1$, with the width of the waveguide smaller than the wavelength, high reflection at the ends of the waveguide up to $R \approx 0.9$ enables uniform longitudinal distribution of the mode intensity.

3. Radiation structure of THz QCL-s
Radiation pattern of THz QCL-s differs drastically from that of the lasers operating at higher frequencies, with transverse dimensions much larger than the wavelength. The small size of laser waveguide leads to a high divergence of output radiation due to diffraction. Additionally we have discovered short range variations in the far field intensity of lasers with sub-wavelength cross section [1], which have not at all been expected based on traditional aperture methods of beam profile calculations used for larger lasers. We developed antenna model of wire lasers, explaining such beam structure by the interference of radiation from longitudinal distribution of sources along the laser waveguide [2]. This theoretical model shows that intensity modulations are accompanied by the rapid change of the phase of the signal, thus leading to drastic decrease of coupling efficiency.

4. Methods of control of radiation structure of THz QCL-s
Several approaches have been proposed by a number of teams worldwide to improve directivity and beam patterns of THz QCL-s. Hyperhemispherical lens placed next to the facet of a wire laser [3] collimates the beam, however it is found to increase the density of interference rings. Considerable improvement of directivity without significant increase
of threshold current has been reached using plasmonic antenna [4] and hollow external waveguide [5]. Surface emission design [6] and integration of a waveguide with horn antenna [7] allowed enlargement of effective aperture and considerable increase of collected power due to improved relation of radiative and non-radiative losses.

We note that interference of radiation from longitudinal distribution of sources being a typical feature of wire lasers is not merely a negative factor when directivity is concerned. Further improvement of beam quality is possible within approaches using specific properties of beam profiles formed by longitudinal interference. Radiation of wire lasers, though non-uniform and divergent, has a regular pattern. This regularity can be used to produce a narrow beam along the laser axis. Our model [2] predicts the possibility to combine small laser aperture and low beam divergence in the case of synchronism of laser mode phase velocity with that of light in air. All the sources along the laser length for such modes emit in phase in the direction of longitudinal axis, producing axially symmetrical beam with the angular width determined by a square root of relation of radiation wavelength to the waveguide length. Such synchronous modes may exist in open dielectric waveguides near propagation cut off. However, intrinsic property of synchronous modes is the vanishing of the parameter of exponential field decay outside the waveguide, leading to low mode confinement.

4.1. External optics for transformation of radiation from Thz QCL-s

Alternative approach is based on the transformation the radiation of a wire laser externally without altering the cavity design and mode losses by means of specially designed lenses. The method is based on the compensation of the phase shifts in the plane perpendicular to the laser axis. Such compensation can be reached using a plate with rings of different optical thickness. This method allows formation of a narrow beam with divergence determined by the relation of the wavelength to the radius of the lens. However only a part of laser radiation can be collected this way, and the optical system requires careful alignment. Using ordinary spherical lens can provide a narrow beam too, as an image of a wire laser located on the lens axis. However, such image may have regions with a dense ring structure of intensity modulations accompanied by rapid phase shifts. Presence and location of such regions depend on the parameters of the laser, the lens focal distance and size, and details of alignment.

4.2. Design of the waveguide using the interference of radiation from longitudinal distribution of sources

Formation of a narrow beam by the interference of radiation from longitudinal distribution of sources from a wire laser is possible without considerable changes to laser mode structure and confinement. It can be realized using periodic modulation of the waveguide. Indeed, there is always a set of points along the waveguide, where emission sources emit in phase in forward direction. Such points are separated by an interval $d = 2\pi/(q - k)$, where $q$ is the longitudinal wave vector of the laser mode, and $k$ is the magnitude of the wave vector of a plane wave in air. Radiation from periodic non-uniformities of the waveguide located in these points can form a narrow beam pattern similar to that of synchronous mode. The power of radiation from such periodic elements does not suffer from destructive interference and thus can be much higher than that of the core of the waveguide. The first low divergence THz QCL waveguide design has been realized using 3-d order DFB providing both the feedback and the resonant scattering forward [8]. Such grating did not provide exact phase matching, and thus had a finite maximum length emitting in phase. Solution of the problem of phase matching of 3-d order DFB has been realized in [9], by insertion of periodic air gaps in the waveguide structure. It should be noted that the output power from high directivity lasers increased several times compared to standard waveguides of similar dimensions. However even greater increase of the output power can be expected with optimized radiation coupling when $\alpha_R = (\alpha_D \alpha_0)^{1/2} - \alpha_0$, where $\alpha_0$ is the small signal gain, $\alpha_R$ and $\alpha_D$ are the coefficients of radiation and dissipative losses respectively. Optimization of radiation coupling can be reached using the system of periodic elements on a distance from a side facet of a laser waveguide. The decay of the field of the laser mode outside the laser waveguide allows control of the level of radiation losses by changing the distance between the laser waveguide and the system of periodic elements, while the feedback can be provided by a separate grating.

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References


FISHNET METAMATERIALS FOR THE TERAHERTZ RANGE

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We report our recent works –modeling, fabrication and experimental characterization using time-domain spectroscopy– on fishnet metamaterials designed for the THz range, which exhibit pronounced left-handed or chiral properties.

1. Introduction

Because of their amazing electromagnetic properties, especially their negative index of refraction, metamaterials are subject to intense fundamental and applied studies, in the whole spectrum ranging from microwaves to the optical domain [1]. Among all possible designs, fishnet structures [2] dedicated to the terahertz (THz) waves are relatively simple to manufacture but they exhibit pronounced left-handed properties. In this contribution, we will describe the recent results we obtained with fishnet samples made of a stack of gold layers perforated with elliptical holes and separated by dielectric layers.

2. Experimental part

2.1 Samples [3]

The alternative stack of gold layers (400-nm thick with 2×20 nm of Cr buffer layers) and dielectric layers (26-µm thick benzocyclobuthene –BCB–) is deposited over a GaAs substrate. After evaporation, a periodical hole array is etched in each gold layer (see Fig. 1). When the whole stack is manufactured, the GaAs substrate is removed under the stack thanks to a deep back-side wet chemical etching, leading to a membrane-like device. Each hole shows an elliptical shape (typical dimensions 225×125 µm²) in order to maximize the THz transmission of the device. The hole periodicity is 340 µm. The first devices of this study (Fig. 1a) are flat homogeneous samples with a thickness corresponding either to 3 or 5 cells (a cell includes a gold layer and a BCB layer) [3]. The second device is a prism-like structure (Figs 1b and 1c): its thickness, i.e. the number of cells, increases along the device length [4]. Finally, the last device (Fig. 1d) is a twisted structure: the in-plane direction of the small axis of the elliptical holes is rotated by 45° from one cell to the one below. This twisted structure is made of 3-cells, thus the small axis is rotated by 90° across the whole device. As transmission through the elliptical holes and coupling between two layers are polarization sensitive, this cholesteric structure is expected to show a chiral electromagnetic response.

![Figure 1: Pictures of a) the metamaterial flat sample and of b) the prism structure. Drawings of c) the prism structure and of d) the chiral device.](https://example.com/figure1.png)

2.2 Set up and characterization procedure

The THz response of these metamaterial samples is obtained from time-domain spectroscopy (TDS), which allows us to get either the reflected, transmitted or deflected signals (amplitude and phase) over the range 0.1-4 THz. To characterize the flat samples (Fig. 1a), we use a classical TDS set up either in transmission or reflexion schemes. The recorded waveforms are Fourier-transformed, and both complex transmission and reflection coefficients are obtained by comparison with a reference signal (transmitted without sample or reflected by a metallic mirror). The THz signal is emitted and received by dipole-type LTG-GaAs photoswitch antennas, excited by fs laser pulses, which are delivering and sensitive to a THz field aligned along the direction of the dipole. To measure the rotation of polarization by the chiral sample, the receiving antenna is oriented at 45° of the emitting one, and the detected polarization is selected with a grid polarizer. As the prism is deflecting the incoming THz beam, we use a goniometric home-made TDS set up to measure the deflection angle. The receiver is located on a rotating arm, and to preserve the requested temporal
coincidence between emission and detection of the THz pulse, the receiving antenna is excited by laser pulses delivered through an optical fibre.

3. Results

Fig. 2-left shows the measured (red points) and calculated (blue curves) modulus and phase of the transmission and reflection coefficients for the flat samples (Fig. 1a). Nearby the first forbidden band at 0.45 THz, the phase is positive, which is the signature of a negative refractive index as seen on Fig. 2 (right). The measured index can be as low as -3 [3]. Let us notice that it is still negative near 0.48 THz, for which transmission is higher than -3 dB.

![Figure 2: – left – Modulus of the a) transmitted and b) reflected THz signals vs. frequency. c) and d) are the respective phases; – right – refractive index for a) a 3-cells and b) a 5-cells thick sample. Red points are experimental data, while blue curves are calculated.](image)

Fig. 3a presents the angular dependence of a Gaussian THz beam deviated by the prism (Fig. 1b) [4]. The dashed line represents the direction normal to the output side of the prism. As expected from the preceding results, the deviation angle is negative for frequencies below 0.5 THz. The continuous line is the incident THz beam shape convoluted by the prism formula with the refractive index as the only adjustable parameter. Fig. 3b shows the prism refractive index versus frequency (measured data and values calculated with different methods). The rotation of polarization induced by the transmission through the chiral sample is depicted on Fig. 3c. Let us notice the very efficient chiral property of this 3-cells slab, since the rotary power is as high as 1000°/λ at 0.5 THz [5].

![Figure 3: a) Angular dependence of the THz beam deflected by the prism for different frequencies. The vertical dashed line indicates the angular limit between left- and right-handed regimes. b) Refractive index deduced from Fig. 3a). c) Rotation of polarization of the THz beam transmitted by the chiral metamaterial.](image)

4. Conclusion

Simple stacks of alternative layers of dielectric materials and metal films perforated with a periodical array of elliptical holes are very efficient metamaterials for the THz frequencies. They exhibit a clearly-observed negative index for given frequency band. First left-handed devices, i.e. prisms and chiral plates, have been fabricated and characterized. New devices for dedicated applications are expected.

References

THz generation by tilted front technique: theory vs experiment

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Comprehensive theoretical and experimental investigation of THz generation by tilted front technique in LiNbO₃ crystal was performed. The role of crystal thickness, pump pulse duration and transverse size on the terahertz generation was analytically demonstrated. Weak and strongly nonlinear regimes of THz generation in LiNbO₃ crystal were experimentally investigated at room and cryogenic temperatures.

1. Instruction

Using tilted-front pump laser pulses was proposed as a way to circumvent the large velocity mismatch between optical pulses and terahertz waves in materials with high optical nonlinearity, such as LiNbO₃ [1]. By using amplified Ti:sapphire laser systems for pumping Mg-doped stoichiometric LiNbO₃ (sLN), this technique has recently resulted in generation of near-single-cycle terahertz pulses with energies as high as 10-125 μJ with a record conversion efficiency up to 0.1% [2-4].

Recently a stationary theory of terahertz emission from a tilted-front optical pulse in an infinite electro-optic crystal was developed [5]. According to the theory, the stationary radiation pattern is, in general, a superposition of the phase-matched wave, the near field of the nonlinear source, and strongly asymmetric Cherenkov cone.

In this paper, we present a dynamic theory of THz generation and its experimental verification. The theory accounts for the transient processes at the entrance boundary of the crystal and, therefore, allows one to trace the dynamics of terahertz field formation in the crystal [6]. The theoretical calculation for conventional scheme, in which a tilted pulse front is introduced by diffracting the pulse off an optical grating and relay-imaging of the pump spot on the grating into the crystal, was performed with account of dispersion and multiphoton absorption of the laser pump. Experimental investigation of terahertz generation in LiNbO₃ crystal was carried out at room and cryogenic temperatures. The effect of laser pulse duration and crystal length for different laser pump energy was investigated.

2. Theoretical and experimental results

In theoretical investigation we assume that a femtosecond laser pulse with tilted intensity front propagates along the x-axis and impinges normally on the entrance boundary x = 0 of an electro-optic crystal. The tilt angle of the pulse is assumed to be α inside the crystal. The FWHM transverse size of the laser beam is L_{FWHM}. The exit boundary of the crystal is cut at the angle α, the thickness of the crystal (along the central line of the laser beam) is L.

To develop an analytical theory, at first, we neglect pump pulse distortions. We introduce the walk-off (Lₜ), build-up (Lₜₒ), and transverse walk-off (Lₜₑ) lengths which characterize the dynamics of THz wave generation in the crystal. In particular, the theory predicts that the THz field amplitude linearly grows with x from x = 0 to x = Lₜₑ. Then the amplitude does not change while the pulse duration increases up to x = Lₜₑ. This amplitude dynamics occurs if THz radiation does not leave region of the optical pump, that corresponds condition Lₜₑ < L_{FWHM}cot(α). If, for example, Lₜₑ > L_{FWHM} the maximum THz amplitude is not achieved. Figure 1(a) shows the radiation patterns calculated for 10 K sLN. It is clearly seen the transient radiation (TR), Cherenkov radiation (CR), phase-matched wave (PMW) and near field (NF). In Fig. 1 the transverse walk-off is L_{FWHM} ≈ 2 mm, Lₜₑ ≈ 0.3 mm and Lₜₒ ≈ 30 mm, i.e., Lₜₑ < L_{FWHM} < Lₜₒ. This means that the amplitude of the phase-matched wavepacket reaches its maximum but the length of packet is not as long as it could be for a wider laser pulse.

To calculate the conversion efficiency and resulted THz spectrum for real experimental setup, we included, using the slowly varying envelope approximation, an important effect of the pulse broadening due to angular and material dispersion as well as mult photon absorption. Moreover, we maximized the efficiency by choosing the position in the crystal where the pulse duration has a minimum. According to Fig. 1(b) increasing the thickness of LN above 2 cm adds little to the conversion efficiency. The optimal pulse duration for LN is ~250 fs.

In the experiment we utilized Ti:Sapphire laser system which provided laser pulses at 795 nm central wavelength with 10 Hz repetition rate, energy up to 10 mJ and typical FWHM pulse duration of 70 fs. During experiment the pulse duration was varied by narrowing optical spectrum in the stretcher. To form laser pulses with tilted intensity front in a sLN crystal we used a conventional setup consisted from a diffraction grating (2000 mm⁻¹), spherical mirror (F=306 mm, D=50 mm) [2]. After diffraction from the grating laser pulse acquired the tilt of the intensity front respect to the phase fronts. This pulse was imaged by the spherical mirror into the sLN crystal situated in the He-cooled cryostat with temperature control. The crystal had a prism-like shape of 7.6x7.6x15 mm size. The laser beam at an entrance facet of the crystal had a FWHM diameter of 4 mm. Generated in the crystal THz radiation was measured by calibrated Golay cell. We also investigated terahertz field spectrum by conventional electro-optic sampling technique in which we used a CCD camera instead of usually used two diodes scheme.
Figure 1: (a) Snapshots of electric field at successive moments for 10K sLN, $\alpha = 60.9^\circ$, $\ell_{FWHM} = 4 \text{ mm}$, $\tau_{FWHM} = 200 \text{ fs}$, and $I_0 = 10 \text{ GW/cm}^2$. (b) The theoretically calculated conversion efficiency as a function of $\tau_{FWHM}$ for sLN, pumped by laser pulses with $\ell_{FWHM} = 5 \text{ mm}$ and $W_{opt} = 0.1 \text{ mJ}$. The crystal thickness and temperature (for sLN) are shown near the corresponding curve.

Figure 2(a) shows optical-to-terahertz conversion efficiency as a function of the optical pump energy for different pulse durations, crystal lengths. It is clearly observed weakly and strongly nonlinear regimes of THz generation. At weakly regime efficiency linearly varied with the optical energy. Maximum growth rate of dependency is obtained for crystal length of 1 cm and pulse duration of 190 fs that agrees with the theory. At strongly nonlinear regime efficiency saturates and even decreases. For all temperatures efficiency saturates at a pump energy level of 0.5–1.5 mJ depending on pulse duration and crystal length. For 77K the efficiency is 3–4 times higher as compare to 300 K and reaches maximum value of ~0.2% for 5 mm and 190 fs. More efficient THz generation for 5 mm crystal length in comparison with 1 cm may be explained by strong pump pulse distortion due to self-interaction in LiNbO3. Terahertz filed oscillogram and spectrum are shown in Fig. 2(b). Spectrum has a maximum near 0.4 THz and extends to 1.5 THz. In experiment we also measured evolution of THz intensity profile at a fix point (see snapshots near time scale in Fig. 2(b)). This evolution demonstrates strong THz beam defraction.

Figure 2: (a) The experimental efficiency as a function of the optical pulse energy for sLN at 77K. (b) The THz field oscillogram and its spectrum (in the inset). The snapshots of transverse intensity distribution are shown near corresponding points at the time scale.

References

SPATIAL PATTERN OF THE PULSED THZ RADIATION EMISSION FROM A TWO-COLOR OPTICAL BREAKDOWN PLASMA

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In this work we study spatial profile of the THz emission from an optical-breakdown plasma using coherent detection in ABCD scheme and noncoherent microbolometer detector array. The spatial profile is found to be conical. Two possible contributions to this profile are discussed.

Plasma of optical breakdown by a two-color femtosecond laser pulses is proved to be one of the most convenient and powerful sources of THz radiation. The emitted THz pulse has an exclusively broad spectrum limited only by the bandwidth of the laser pulse, i.e. its duration [1]. Thus, the 120 fs pulse can be used for generation of 0-8 THz single-cycle pulses. Characterization of spatial and polarization properties of the emitted radiation is necessary for numerous applications of plasma as a source of THz pulses. In this work we present the investigation of spatial and polarization profile of the emitted THz radiation using three independent detection techniques: non-coherent detection of THz pulse energy using a Golay cell, imaging of the focused THz beam with a microbolometer detector array [2] and coherent time-domain measurement of the electric field using ABCD technique [3].

Theoretical description of the THz pulse generation comprises several contributing processes which act simultaneously and predict different properties of the terahertz radiation. We can divide these contributions into two groups: single-electron mechanisms and collective motion mechanisms. The single-electron processes include the four-wave mixing on the third-order nonlinearities of neutral atoms in main or excited states, and the photoionization process which leads to generation of photocurrent in the beam waist region [4]. Both of these mechanisms result in forward-directed THz emission with polarization defined by polarizations of fundamental and second harmonic pulse and phase difference $\psi$ between them. The collective motion mechanisms include transformation of the plasma oscillations into the radiation in the far zone due to non-uniform plasma density profile and radiation due to the charge separation by the ponderomotive force of the focused laser beam. These mechanisms lead to the emission of THz radiation directed into a cone with “radial” polarization distribution.

Figure 1. Pattern of THz radiation registered with a microbolometer antenna array beyond the focus of THz beam

In the experiment and simulations we used Ti:Sa laser pulses at the wavelength $\lambda_0=0.8$ µm with duration $\tau_{\text{FWHM}}=120$ fs and the pulse energy up to $W_l=1.0$ mJ.

A microbolometer detector array was used for visualization of the spatial profile of the THz radiation. It provided a 320*240 image of the THz radiation when placed close to the focus of the THz beam. The pattern of THz radiation transformed from a point to a ring structure when the detector was moved away from the focal plane of the THz beam. The ring size suggested a conical spatial profile with vertex angle $\theta=17^\circ$.

Another study of the spatial profile was carried out using a time-domain ABCD detection scheme. An iris diaphragm was used to obtain spatial resolution. It is clearly seen from the figure 2 that the THz pulse is directed into a cone. Lower frequency components of the THz pulse propagate into a wider angle and higher frequency components propagate closer to the axis of symmetry.
Figure 2. Pattern of the THz radiation registered with a microbolometer antenna array beyond the focus of THz beam.

In conclusion, we claim that the THz radiation from a plasma of a two-color femtosecond laser pulse breakdown of air has a conical spatial profile with lower frequency components directed into wider angle. We suppose two possible contributions to the conical profile. The first is the transition radiation emission from that the spatially confined laser spark with relatively sharp plasma density gradient at its edges. The second contribution originates from a forward-directed dipole radiation profile of the microscopic drift photocurrent affected by the reflection from the dense plasma in the vicinity of the axis of propagation.

References


ULTRA-SHORT LASER ABLATIVE BASED SYNTHESIS OF COLLOIDAL NANOMATERIALS FOR BIOLOGICAL APPLICATIONS

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The presentation will overview a series of laser ablative methods for the synthesis of colloidal nanoparticles, which were recently developed in our Institute. The methods imply the use of ultra-short laser radiation to ablate either a solid target or water-dispersed particulates in aqueous environment in order to produce ultrapure nanomaterials. Particular attention is given to the synthesis of plasmonic (Au, Ag) and semiconductor (Si, ZnO) nanostructures. Having much superior purity compared to chemically synthesized counterparts and exhibiting promising optical properties, the nanomaterials present unique objects for biological applications such as biosensing, drug vectoring, imaging and therapeutics.

Inorganic nanoparticles (plasmonic nanoparticles, semiconductor-based quantum dots etc) are known to offer novel promising properties for biological sensing and imaging, as well as for therapeutics. However, these applications are often complicated by potential toxicity issues, arising as a result of inadequate purification procedures of nanoparticles obtained via synthetic pathways using toxic or non-biocompatible substances. As an example, despite natural biocompatibility and biodegradability, Si nanoparticles cannot be chemically produced in pure state, as all chemical synthesis routes inevitably lead to their contamination by toxic by-products (HF derivatives etc). Pulsed laser ablation in liquids has recently emerged as a novel “green” tool for synthesis of colloidal nanomaterials, which offers a breakthrough in the solution of the toxicity problem. In this method, laser radiation is used to ablate a solid target in liquid ambience to form nanoclusters, which are then released into the liquid forming a colloidal nanoparticle solution. A huge advantage of this “physical” synthesis route consists in its independence on colloidal chemistry that enables one to avoid the employment of toxic substances or by-products. Indeed, nanomaterials are directly created from the bulk state, while the fabrication procedure can be carried out in clean environment (deionized water or aqueous biocompatible solutions).

This presentation will review our on-going research activities on laser ablative synthesis of nanomaterials. Our approach consists in the employment of ultra-short (ps, fs) laser radiation for both laser-ablative nanofabrication and secondary fragmentation of already formed nanoparticles. This makes possible a purely physical control of size characteristics of synthesised nanomaterials (the size can be tuned from few nm to hundreds nanometers) and the reduction of nanoparticle size dispersion. In addition, taking advantage of unique surface chemistry and reactivity of laser-synthesized nanomaterials, we employ different chemical substances (biopolymers, oligosaccharides etc) to control the growth of nanoparticles and functionalize their surface for various applications. In particular, such approach can lead to formation of unique nanostructures without any intermediate group, as, for example, in cases of Au nanoparticle – Polyethylene Glycol (PEG), Au nanoparticle – dextran or Au nanoparticle – Cyclodextrin complexes, suggesting the involvement of new chemical principles associated with “bare” nanomaterial surfaces. Exhibiting unique purity in the absence of even a trace of contaminant, the synthesized nanomaterials look extremely promising for biological imaging and therapeutics and are now tested in cancer research.
THIN FILMS GROWTH BY SOFT PULSED LASER TECHNOLOGIES FOR APPLICATIONS IN DRUG DELIVERY, IMPLANT COATING AND BIOSENSING

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We review new results on the synthesis of thin films for various biomedical applications by Matrix Assisted Pulsed Laser Evaporation (MAPLE) and Laser Direct Writing (LDW).

Implant coatings

We produced by MAPLE biomimetic inorganic-organic thin films of hydroxyapatite (HA), the inorganic component of the bony tissues, and a natural biopolymer — silk fibroin (FIB) — added for surface functionalization. Compared to the simple FIB or HA thin films, we observed that the composite HA-FIB coatings, with micronic droplets forming an extended surface, favorable to bone cells anchorage and proliferation. Osteosarcoma SaOs2 cells cultured 72 h on FIB and HA-FIB films showed increased viability, good spreading and normal cell morphology. The well-elongated, flattened cells were a sign of an appropriate interaction with the FIB and composite HA-FIB coatings.

Octacalcium phosphate (OCP) is a promising alternative to HA as biomaterial for hard tissues repair. Magnesium substituted OCP and Strontium substituted OCP deposited by MAPLE on Ti substrates enhance osteoblast activity and differentiation. The increased proliferation, and superior activity and differentiation of the cells grown on SrOCP and MgOCP with respect to those cultivated on undoped OCP films or on polystyrene plate controls demonstrated that ion-doping improves the beneficial effect of OCP on bone cells, suggesting that MgOCP and SrOCP coatings could be usefully applied on Ti implants for orthopedic use. The production of procollagen-type I, transforming growth factor-β1, alkaline phosphatase and osteocalcin indicated that the level of differentiation of the cells grown on the different coatings increased in the order OCP < MgOCP < SrOCP.

We present an exhaustive characterization of fibronectin (FN) — an extracellular matrix protein with important roles in tissue repair and wound healing — patterns obtained by LDW onto accepting titanium substrates trough UV nanosecond laser transfer assisted by a thin sacrificial metallic layer. FTIR investigations demonstrated that the secondary structure was generally unchanged after the transfer, while the Western Blot results indicated the molecular weight preservation. Thermal-sensitive regions of the protein molecule, such as the cell binding domain on glycosylations were equally preserved during the transfer, as demonstrated by the specific anti-RGD and glycosylations staining. The most important, the in-vitro experiments showed that the FN preserved its biological functionality towards two representative cellular lines, i.e. MCT3T osteoblasts and Swiss 3T3 fibroblasts. This opens the door to the applicability of the LDW technique in obtaining hybrid complex nanostructures for use in both bone and dermatological tissue regenerative engineering.

Thin films of vitronectin (VN), an extracellular matrix protein with distinctive active domains for cell attachment and signalization, were obtained from a cryogenic aliquot obtained by freezing a protein-saline buffer solution. The stability
and integrity of VN after MAPLE transfer was shown by their interaction with human osteoprogenitor (HOP) cells in which actin filaments stretched across the entire cell area and clear focal points with surface were formed.

**Biosensing**

We synthesized nanostructured Zn(II)- and Co(II)-metalloporphyrin MAPLE thin films onto silicon wafers, quartz plates and screen-printed electrodes. The sensitivity to dopamine of the Zn(II)- and Co(II)-metalloporphyrin thin films on screen-printed carbon nanotube electrodes was evaluated. The best sensing properties were obtained in case of thin films of Co metalloporphyrin.

We produced by MAPLE metalized nanostructured (5,10,15,20-tetraphenyl)porphinato manganese(III) chloride thin films onto gold screen-printed electrodes or <111>Si substrates. The deposited nanostructures exhibited globular structures with average diameters decreasing with laser fluence. We have investigated the films by cyclic voltammetry in order to evaluate the potential bio/chemosensing activity on dopamine neurotransmitter analyte. It was found that the manganese(III)-porphyrin is appropriate as a single mediator for dopamine sensing in the specific case of gold screen-printed electrodes.

We fabricated by LDW mesotetraphenylporphyrin micropatterns on Si substrates. The propulsor metal film thickness was found to be a key parameter, which determines the laser fluence range allowing the clean transfer, predominant mechanism of the blister formation and laser-induced heating of the transferred material. The target with 1.5 μm thick titanium film provided negligible heating of the porphyrin transferred by laser pulses.

**Controlled drug delivery systems**

Thin films of poly(1,3-bis-(p-carboxyphenoxy propane)-co-sebacic anhydride)) 20:80 thin films containing several gentamicin concentrations were manufactured. Release of gentamicin from these MAPLE-deposited polymer conjugate structures was assessed. The activity of gentamicin-doped films against *Escherichia coli* and *Staphylococcus aureus* bacteria was demonstrated using disk diffusion and antibacterial drop test.

We produced thin films of levan on glass and Si wafers from solutions of pure exopolysaccharides in dimethyl sulfoxide. The MAPLE structures were compact with high specific surface areas. The contact angle studies evidenced a higher hydrophilic behavior in the case of oxidized levan structures because of the presence of acidic aldehyde–hydrogen bonds of the coating formed after oxidation. In-vitro colorimetric assays revealed a high potential for cell proliferation for all coatings with certain predominance for oxidized levan.

Iron oxide nanoparticles were prepared by chemical co-precipitation method. The nanoparticles were mixed with dextran in distilled water. The obtained solutions were frozen in liquid nitrogen and used as targets during MAPLE for the growth of hybrid, ironoxide nanoparticles-dextran thin films. The biocompatibility of the iron oxide-dextran thin films was demonstrated by 3-(4,5 dimethylthiazol-2-yl)-2.5-diphenyltetrazolium bromide-based colorimetric assay, using human liver hepatocellular carcinoma cells.
PICOSECOND LASERS IN STRUCTURING OF THIN FILMS FOR PHOTOVOLTAICS

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Abstract

Progress in picosecond lasers during the recent few years made them a reliable tool for microfabrication of diverse materials. Their benefits are especially evident when cost-effective solutions are required in processing of thermally sensitive layered structures. Laser scribing is an important step to preserve high efficiency of thin-film photovoltaic devices over large areas by production of monolithic interconnects. Review of the current state-of-the-art and our results on picosecond laser application in the CuInGa(1-x)Se2 solar cell scribing with different wavelengths and beam profiles are presented. Experimental work was supported by modeling and simulation of energy coupling and dissipation inside the layers. Selectiveness of the ablation process is defined by optical and mechanical properties of the materials. Both the wavelength and the beam profile are of essential importance for the selectivity of the laser ablation process and for its efficiency. The scanning electron microscopy, electron-dispersion spectrometry, micro-Raman and lock-in thermography have been used to evaluate the processing results to show benefits of the used picosecond lasers in selective scribing on this type of photovoltaic structures. Utilization of the whole laser power by parallel processing and use of spatially shaped laser beams of high repetition rate lasers with the picosecond pulse duration offer new possibilities for high quality and efficiency patterning of advanced materials for photovoltaics.

1. Lasers and thin-film solar cells

Efficiency of the thin-film solar cell with a large active area might be maintained if small segments are interconnected in series in order to reduce photocurrent in thin films and resistance losses. There are no established processes for laser scribing of CuInGa(1-x)Se2 (CIGS) solar cells due to thermal sensitivity of the absorber material. Most of research using picosecond lasers in scribing CIGS solar cells was performed with layers deposited on a rigid glass substrate[1, 2, 3]. The laser scribing processes of CIGS on flexible metal and polymer substrates[4, 5] are still challenging. Moreover, the effect of laser scribing on photo-electrical performance of the processed thin-film CIGS photovoltaic structures is rarely addressed.

Our research was concentrated on development of the P3 process, scribing of films to expose the molybdenum back-contact by selective removal of both the top-contact and CIGS layers, as it is the most difficult laser process in production of this type solar cells. The picosecond laser was selected for the experiments because the short pulse duration can prevent the thermal damage and degradation of the materials, enabling selective high quality ablation of the films.

2. Experimental setup and samples

Experimental setups for the laser scribing experiments included the picosecond laser (Atlantic, 10 ps, 100 kHz, EKSPLA). Non-linear crystals were used for conversion of the 1064 nm wavelength generated by the laser to 532 nm, 355 nm or 266 nm radiation. An optical parametric generator was used to convert the laser radiation to the 1572 nm wavelength. Complete flexible multilayer structures of the CIGS Solar cells with three different top contacts were used in experiments. The samples were prepared by Solarion AG, Germany.

3. Modeling of energy coupling and laser induced stress

Selectiveness on laser processing in multilayered structures the only possible if the energy coupled in a well defined volume at the interlayer interface and selection of the right laser wavelength is important. Therefore, the finite element method was applied to simulate the process, including laser energy coupling by electrons, evolution of electron and lattice temperature according to the two-temperature method and stress induced by rapid local heating of the materials. All simulations were performed for three different CIGS solar cell structures as well as for a set of laser wavelengths available at the laboratory. Laser energy coupled inside the films can be found by solving the beam propagation equation which takes into account absorption and reflection of electro-magnetic waves in the layers. Its solution was the energy locally coupled from an incident laser pulse inside the material stack. UV radiation at 266 nm was absorbed in a thin layer close to the outer surface of ITO and selectivity of the ablation process is hardly to be expected. The infrared light can reach the molybdenum back-contact. Localization of the coupled energy at inner interfaces is a key to control selectivity of laser scribing process.

Numerical simulation of the temperature distribution in the CIGS solar cell structures after absorption of a laser pulse was followed in order to find out removal mechanisms of the transparent conductor and CIGS layers depending on the wavelength of laser radiation. Evolution of electron and lattice temperatures inside the layers was simulated using the two-temperature model. For the infrared radiation, the high temperature of the molybdenum surface and good
selectivity of CIGS layer removal can be predicted because the laser radiation penetrates through the absorber and is well absorbed at the CIGS-Mo interface. Rapid temperature increase leads to local thermal strain and resulting stress within different layers in the range of tens of GPa, which is high enough to initiate spallation of the top layers.

4. Scribing results using picosecond laser

Scribing of the CIGS structure with the thick ITO top-contact was performed with different wavelengths from the picosecond laser. Use of the high average laser power to scribe the ITO/CIGS films with the 532 nm radiation in a single scan led to the ITO layer peeling off in a wide area (width ~30 µm), while exposure of the Mo film by CIGS ablation was only 6 µm wide. A smooth scribe was achieved using 10 times reduced laser power and multiple scans. UV radiation absorbed close to the surface and layer-by-layer ablation took place using multi-scan scribing. The 1064 nm laser wavelength was found to be optimal for the P3 type scribe formation in the thin film CIGS structure. It is very positive result in case of industrial applications as the cost and system complexity are decreased. By increasing the scanning speed up to 900 mm/s, it was possible to selectively remove only the ITO layer without any remarkable influence on the absorber layer underneath.

![Figure 1. Detailed SEM view on the edge of the P3 laser scribe in CIGS structures: a) 1572 nm, 800 mW, 50 kHz, 200 mm/s, single pass; CdS/CIGS/Mo/PI; b) 355 nm, 100 mW, 50 kHz, 2 µJ, 300 mm/s, 20 loops; ZnO:Al/ZnO/CdS/CIGS/Mo/PI.](image)

5. Characterization of laser scribing in CIGS solar cells

The quality of processing was evaluated with an optical and scanning electron microscopes. Profiles of the laser ablated holes and trenches and chemical composition of the resulting surfaces were evaluated with the x-ray energy dispersion spectrometer (EDS) and micro-Raman spectrometer. Lock-in thermography (LIT) and Laser Beam Induced Current (LBIC) techniques were applied in the area near the scribes to detect any short-circuiting caused by laser ablation. The photo-electrical efficiency measurements were performed on complete working solar cells of prefabrication stage with an active area of 32 cm² at irradiance using the standard global spectra AM 1.5 and 1000 W/m² intensity. The total length of laser scribes was 360 mm in all cases. The photo-electrical efficiency and parallel resistance measurements were performed on cells used in laser scribing before and after the processing. The efficiency tests after laser scribing showed a minor decrease in solar cell performance and parallel resistance during laser scribing with both pulse durations. The average drop in efficiency of CIGS solar cell after laser scribing was by 0.35% from initial average value of 10.7%.

6. Conclusion

Selectiveness of the laser scribing process is one of main parameters for applications of the technology in thin-film electronics, including photovoltaics. Selection of the proper laser wavelength is important to keep the energy coupling in a well defined volume at the interlayer interface and this can be a way to achieve selective removal of layers even in the front-side irradiation geometry, which is only acceptable for solar cells on flexible substrates. The solar cell efficiency tests revealed minor degradation in photo-electrical efficiency when the picosecond laser scribing was applied to the solar cell samples. Lock-in thermography measurements did not revealed any internal shunt formation during laser scribing with picosecond pulse duration.

References

NANOSTRUCTURE FORMATION ON SOLID SURFACES MELTED BY LASER PULSE

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Abstract

The paper describes the model of nanostructure formation on solid surface by nanosecond laser pulses melting the material. Stefan problem with corresponding boundary conditions is solved in combination with nucleation theory. It is found that typical size of surface nanostructure formed depends on energy and duration of laser pulse. For comparison of theoretic and experimental results various industry material (germanium, titanium, zirconia dioxide) pieces irradiated by ArF-laser are shown.

1. Introduction

In recent years nanostructures in solids have been attracting ever greater attention from researchers because they are promising objects for applications in various fields of science and engineering. Both ordered and disordered ensembles of nanoparticles are new artificially created materials whose widespread use is associated with their unique properties. In this work we study the mechanism responsible for the formation of nanostructures at the surface of solids under the action of nanosecond laser pulses. Two parts can be mentioned by the solution of this task. In the first part, the process of material melting occurring as a result of laser impact is being considered and the Stefan problem with the corresponding boundary conditions is being solved. In the second part, the process of a melted layer cooling at the expense of heatsink into the solid phase bulk together with a theory explaining the formation of crystalline seeds is being considered [1]. As a result, we obtain the expression for the characteristic size of nanostructures depending on the pulse duration and energy. To compare calculated and experimental data, we study the action of pulses of an ArF laser with a wavelength of 193 nm on the surface of a number of widely used materials (titanium, germanium, zirconia dioxide).

2. Model of nanostructure formation

2.1 Melting stage

Surface layer begins to melt if energy density and width of laser pulse are high enough. When laser pulse ends, surface layer cool down and freeze by means of heat transmission into solid phase [2].

Consider a semi-infinite one-dimensional block of metal at initial temperature \( T = T_{in} \) for \( x \in [0, \infty] \). The metal is heated with heat flux of pulsed laser radiation. The flux causes the metal to melt down leaving an interval \([0, y(t)]\) occupied by metal melt, where \( y(t) \) is moving boundary of two phases (liquid and solid). Using heat equations for each phase with corresponding boundary conditions we have

\[
\frac{\partial^2 T_1}{\partial x^2} - \frac{1}{a_1} \frac{\partial T_1}{\partial t}, 0 < x < y(t), \quad (1)
\]

\[
\frac{\partial^2 T_2}{\partial x^2} - \frac{1}{a_2} \frac{\partial T_2}{\partial t}, y(t) < x < \infty, \quad (2)
\]

\[
T_2(x, 0) = T_2(\infty, t) = T_{in}, \quad (3)
\]

\[
\frac{\partial Q(t)}{\partial t} = -\lambda \frac{\partial T_1}{\partial x} \bigg|_{x=0}, \quad (4)
\]

\[
T_1|_{x=y(t)} = T_2|_{x=y(t)} = T_k, \quad (5)
\]

where \( a, \lambda, c \) are temperature conductivity, thermal conductivity, and specific heat capacity correspondingly; \( \rho \) is a material density; \( Q(t) \) is an energy absorbed per unit area during \( t < \tau \), where \( \tau \) is a pulse duration; \( T_k \) is a melting temperature. Liquid phase is denoted by number 1, solid phase is denoted by number 2.

Making certain simplifications [1] and solving this system of equations we get transcendental equation to define \( \beta \):

\[
2c\rho(T_k - T_{in}) \sqrt{\frac{a}{\pi}} = \left[ \frac{1}{\sqrt{2\pi}} \exp \left( \frac{\beta^2}{2a} \right) - 2 \right] + \frac{Q(\tau)}{\sqrt{\tau}} \text{erfc} \frac{\beta}{\sqrt{2a}}, \quad (6)
\]
This parameter $\beta$ allows us to calculate melting depth of different materials irradiating with laser pulses of various duration and energy.

2.2 Crystallization stage

After laser pulse ends a phase transition process starts. Liquid phase transforms into solid one. The crystallization with nanostructure formation occurs if cooling rate of molten metal is high enough [2]. To determine the cooling rate we need to solve the problem of molten layer cooling into solid phase.

Using variation principle in basic heat conduction law [3] and kinetic equation in nucleation theory [4] we obtain the size of nucleating center of solid phase in supercooled liquid:

$$r(t) = v_0 d \exp \left( \frac{U}{kT_0} \right) \frac{kT_0^2}{U} \left( \frac{h}{U+h} - \exp \left( - \frac{U}{kT_0^2} \right) + \frac{1}{U+h} \exp \left( - \frac{e(U+h)}{kT_0^2} \right) \right) r 
- R \left( 1 - \exp \left( - \frac{U}{kT_0^2} \right) \right)$$

(7)

where

$$R = \frac{v_0 d \exp(-U/kT_0) kT_0^3 h}{eU(U+h)}.$$

3. Experiment

The formation of micro- and nanostructures were observed on specimens of titanium, germanium and ceramics based on zirconia dioxide at a multipulse irradiation by nanosecond (20 ns) ArF-laser with wavelength of 193 nm. The analysis of irradiated surface profiles is carried out by an atomic-force microscope (AFM). For example figure 1 shows the specimen of germanium.

![Figure 1: 3D photograph of relief in the peripheral low-intensity region at the titanium surface after irradiation by nanosecond ArF-laser with wavelength of 193 nm](image)

4. Conclusions

The model for estimating the characteristic sizes of nanorelief formed on the solid surface as a result of melting by laser pulses is developed. It is denoted the dependence of the cooling rate and characteristic sizes of nanorelief on the duration and energy of the laser pulse. This indicates the possibility of controlling the processes responsible for the formation of nanostructures. Investigations with the help of an atomic force microscope have proven the formation of the nanorelief at the surface of germanium as a result of the action of nanosecond pulses of an ArF-laser with a wavelength of 193 nm.

References

Micro processing with ultra-short pulses: Influence of the pulse duration on the removal rate and the machining quality

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Abstract

Ablation characteristics in the range of 10 ps to 50 ps for 1064 nm wavelength are well known [1, 2]. With increasing pulse duration, the removal rate decrease and also the quality suffers for metals and silicon. In this work results for ablating metals, semiconductors and isolators with pulse durations from 250 fs to a few ps are reported. The ablation characteristics for different wavelength were studied.

1. Introduction

The interest in ablation with ultra short laser pulses has strongly increased since industrially applicable laser systems with pulse durations around 10 ps have been available. During the last years progresses in the development of further industrial suited ultra short pulsed laser systems have been made, on the one hand towards shorter pulse durations down to a few hundred fs and on the other hand towards more cost effective fiber based systems with pulse duration of a few tens ps. However, beside the quality improvements which can be achieved with ps and fs pulses, also the process efficiency denotes a key factor for the successful transfer of this technology into real industrial applications. The process efficiency is directly influenced by the material removal rate per average power (i.e. the ablation efficiency), which is influenced among others by the pulse energy, the pulse duration and the wavelength. These parameters are accessible by the choice and the operation mode of the laser system. For almost all kind of materials it has been found, that at the wavelength of 1064 nm the ablation efficiency decreases when the pulse duration is raised from 10 ps to 50 ps [1, 2]. A second scaling factor for industrial applications is the achievable quality which scales directly with the appearance of melting residues. In literature it is shown that the quality of the ablated surfaces seems to be better with shorter pulses [2-4].

2. Experiments

The ablation behaviors for copper, silicon, germanium, soda-lime glass and fused silica are investigated by ablating squares and lines. The depth of the squares directly scales with the material removal rate which describes the ablated volume per time and average power. With the removed volume of the lines, the material removal rate can be calculated with the marking speed. The used pulse durations range from 250 fs to 10 ps. The used laser has a wavelength of 1026 nm. Experiments with the second harmonic of 513 nm were machined, as well.

3. Results

3.1 Metals

Corresponding to [5-8] at 1026 nm an increase of the removal rate with decreasing pulse duration for copper is observed. This increase is mainly caused by the change of the energy penetration depth (Fig. 1a). In the case of 513 nm the decrease of the removal rate in the range from 250 fs to 2 ps is less pronounced compared to 1026 nm in the same range of pulse duration. For the second harmonic a nearly constant energy penetration depth could be observed. Therefore the dependence of the removal rate from the pulse duration is only weak which is also confirmed by other experiments.

Figure 1: Material parameters for copper and 128 applied pulses; a) Threshold fluence; b) Energy penetration depth
3.2 Semiconductors
Between undoped and doped silicon no differences could be observed. Germanium, which has a smaller Band Gap, shows the same tendency (Fig. 2a,b). With the same laser parameters the squares in Germanium are deeper. On the one hand the threshold fluence is smaller for germanium than for silicon. On the other hand the energy penetration depth is higher for germanium. These two factors lead to deeper squares in germanium. For both materials a Crater and Cone formation can be observed at the ground of the squares which constrain the microscopy measurements.

3.3 Transparent isolators
The investigated transparent materials are soda-lime glass and fused silica. For soda-lime glass a rapidly increase of the squares depth is observed at a certain pulse duration (Fig. 3a). This pulse duration depend on the wavelength and the laser peak fluence. The reason could be a change of the absorption process for longer pulses. For longer pulse duration it seems that the ablation process is supported by a mechanical process to break-off the material. In the case of fused silica, the structure depth is almost constant. The depth of the squares rest at a certain level, which depends on the laser peak fluence and the wavelength.

3.4 Nontransparent isolators
Polycrystalline diamond (PCD) shows the same tendency as copper. A decrease of the removal rate for longer pulses at 1026 nm and a nearly constant removal rate at 513 nm. Zirconium oxide, as a second electrical isolators shows a rapidly decrease with increasing pulse duration for the IR. For 513 nm the removal rate is again nearly constant.

References
LASER EMBRYOLOGY: APPLICATION OF ADVANCED LASER TECHNOLOGY FOR MICROMANIPULATION AND DIAGNOSTICS OF FUNCTIONAL STATE OF EARLY MAMMALIAN EMBRYOS

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Novel method of laser micromanipulations with early mammalian embryos has been demonstrated, including moving, fusion, microsurgery, etc. The development of this method allows increasing the mammalian cloning efficiency. In this work Infrared pico- and femto-second lasers were used for the inactivation (functional enucleation) of oocytes and two-cell mouse embryos and for the fusion of blastomeres of two-cell mouse embryos. Artificial fusion of cells is a powerful research tool for various biotechnological experiments with mammalian gametes and embryos. However, the existing methods have serious disadvantages and limitation. In our experiments we have developed and demonstrated the use of laser beam for the fusion of various embryonic cells of different size and of two or three blastomeres inside of four-cell mouse embryos without affecting the embryo’s integrity and viability. The lasers technologies also were used for diagnostics of state of early mammalian embryos. The Raman microspectroscopy and Raman mapping as well as lifetime imaging autofluorescence of mitochondrial NADH of embryo was used for embryo state analysis. These methods allow with high spatial resolution and high sensitivity studying the structure and molecular processes in the cells.

1. Introduction

Modern nuclear transplantation methods may have a significant adverse effect on cells, resulting in low survivability and high failure rate in the development of cloned organisms. The reconstruction of mammalian embryos involves a series of complex step-by-step microsurgical manipulations including (1) the preparation of the recipient cytoplast by the elimination or inactivation of the genome of the recipient cell (oocyte or zygote), (2) the insertion of a karyoplast or a whole somatic cell under the zona pellucida of the cytoplast with microinstruments; this procedure is the least traumatic for the operated cells, and (3) the electrofusion of the karyoplast and cytoplast. These steps may have an adverse impact on the development of embryos have an adverse impact on the development of embryos [1]. Particularly, electrofusion usually performed in special dielectric media, which may affect the development of embryos. Also electrofusion drastically changes the intracellular homeostasis in the reconstructed embryos [2] as a result of electrical breakdown and formation of temporal pores not only in the cell-cell contact area but also over the entire membrane surface [3]. In the present work, we report the first successful demonstration of all-optical laser nuclear transfer in mouse embryos involving the 3 steps listed above without any mechanical micromanipulations and microsurgical instruments. Used method of fusion in contrast to other ones allows selective fuse inside embryo chosen area (e.g. inside four cell embryo we can fuse two or three of them, without disturbing the others or fourth one). Modern laser optical methods are also widely used for observation, analysis, control of biological cellular systems however limited number of works concern researches and development these methods for mammalian embryos. We have applied methods of Raman spectroscopy as well as lifetime imaging autofluorescence of mitochondrial NADH of embryo was used for embryo state analysis. These methods allow with high spatial resolution and high sensitivity studying the structure and molecular processes in the cells.

2. Experimental Methods

The femtosecond and picosecond tunable Ti:Sapphire lasers “Tsunami” (Spectra Physics) with high repetition rate (about 80 MHz), combined with Olympus IX71 invert microscope were used in the experiments. For micromanipulation and microsurgery a shutter was used to cut off the light beam with necessary time duration for treatment (fusion and enucleation). Controlled motion stage was used for precise positioning cells under the beam. For fluorescence lifetime imaging microscopy (FLIM) of enzymes we used homemade scanners systems, on the base of 2D galvano-scanner (Raylase) and photon counting detector SPD-5C (MPD) combined with above mentioned microscope and lasers. Time-Correlated Single Photon Counting System PicoHarp 300 and SymPhoTime software from PicoQuant were used for data counting and analyses. For Raman spectroscopic analysis α-SNOM WITEC (Germany) microspectrometers was used, equipped with laser 488 nm (MellesGriot 43 Ion Laser), using objective Nikon Plan 100x/0.90. The study was carried out on embryos prepared according to [4].
3. Results and Discussion

We have successfully demonstrated the feasibility of non-destructive laser fusion and enucleation of mouse embryos using only pulse laser without any mechanical contact [4]. In our experiments (1) laser enucleation of oocytes with subsequent laser perforation of the zona pellucida; (2) laser capture and transfer of somatic (cumulus) cells under the zona pellucidal, and (3) laser fusion of oocytes and somatic cells have been done. The oocytes were inactivated (enucleated) with single irradiation of a pronucleus with a laser pulses of average power of 0.1–0.3 W and duration of 0.3 s, focused on one of the pronuclei. After enucleation, selective zona pellucida perforation was irradiated with a single laser pulse (with an average power of 240 to 300 mW and a pulse duration of 800 - 1000 µs). The diameter of resulting opening was 12 to 15 µm. The laser capture and transfer of cumulus cells (diameter ~ 7 to 9 µm) under the zona pellucida, was performed using continuous radiation mode at optical power ranging from 20 to 30 mW. We also have demonstrated fusing the oocyte with the polar body, which is similar in size to the somatic cell and has a natural tight contact with the oocyte membrane.

We have shown that the laser inactivation of both blastomeres of two-cell mouse embryos by irradiation of nucleoli completely blocked further development of the embryo. The inactivation of one blastomere, however, did not affect the ability of the second intact blastomere to develop into a blastocyst after treatment. Laser inactivation of oocytes at Metaphase II (MII) stage and of parthenogenetically activated pronuclear oocytes also completely blocked their ability for further development. Suitable doses of irradiation in cytoplasm region did not affect the ability of embryos and activated oocytes to develop into a blastocyst.

Same method was used for the fusion of two or three blastomeres inside four-cell mouse embryos without affecting the embryo integrity. We demonstrated by Hoechst 33342 staining the successful fusion of the blastomeres by showing two or three nuclei in one cytoplast. The viability of the treated embryos was estimated by in vitro cultivation till blastocyst stage. The ability of non-treated embryos in control groups to reach the blastocyst stage was about 80 %. The methods to estimate the embryo state on the base of FLIM and Raman are developed. It was shown that Raman spectra from embryos reveal set of characteristic peaks; the spectra peaks positions, relative intensities as well as their spatial distribution depend on the cell type and state. FLIM of mitochondrial NADH of embryo also was measured. These measurements allow develop the methods to precisely estimate the quality and viability of individual embryos.

Obtained results demonstrate unique opportunities of the applications of a suitable infrared periodic pulse laser as a universal microsurgery tool for individual living cells [4]. It is known that, after electrofusion (as a result of electrical breakdown of membranes), a certain percent of fused cells may die within the next 2 to 3 hours of culturing in vitro. In our experiments on laser fusion of oocytes cultured in vitro, no destruction of fused oocytes was observed. In optical laser microsurgery it is not necessary to use any glass microinstruments and mechanical micromanipulators which can cause serious traumas in the operated cell. The laser fusion, in contrast to electrofusion, does not require special operation chambers and special media and can be performed in the standard M2 medium that is commonly used for embryos manipulations. In the case of laser fusion, the laser beam affects the membranes only at the restricted focal region and do not cause any serious disturbance to ion homeostasis, which was often observed in electrofusion. In summary, we have successfully demonstrated for the first time, the non-invasive all-optical laser nuclear transfer in mouse embryos without any mechanical contact; appropriate modifications and further improvement of this approach may lead to promising practical applications in therapeutic and reproductive cloning, and microsurgical correction of embryonic diseases [5].

4. Acknowledgments

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LASER PHOTOCHEMISTRY OF MOLECULAR OXYGEN. APPLICATION TO STUDIES OF OXYGEN ABSORPTION SPECTROSCOPY IN SYSTEMS OF CHEMICAL AND BIOLOGICAL IMPORTANCE.

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Short abstract. The IR absorption spectra corresponding to the singlet-triplet transitions in O₂ molecules dissolved in organic solvents and water have been estimated under ambient conditions, using oxygenation of singlet oxygen traps upon direct laser excitation of oxygen molecules. The optical densities and molar absorption coefficients for the absorption bands at 765, 1073 and 1273 nm were obtained. The data are compared with the luminescence spectra and radiative lifetimes corresponding to the singlet-triplet transitions in O₂ molecules. Significance of the obtained spectroscopic data for biomedical research is discussed.

Oxygen molecules are triplet (\(^3\Sigma_g^–\)) in the ground state and have two low-lying singlet states \(^1\Delta_g\) and \(^1\Sigma_g^+\). Luminescence of singlet oxygen in the solution phase has been studied in detail. The absorption bands corresponding to the triplet-singlet transitions in dissolved oxygen molecules are studied much worse because these bands are very weak. Therefore, they cannot be detected using conventional spectrophotometers under ambient conditions. The absorption spectra were recorded only at very high oxygen pressure (100-150 atm.). At this pressure, the absorption spectra are mostly determined by dimols (dimers) of oxygen molecules. Recently, we developed a simple photochemical approach to investigation of the absorption bands of molecular oxygen dissolved in organic solvents and water at normal atmospheric pressure. This method is based on measurement of photooxygenation rates of singlet oxygen traps (1,3-diphenylisobenzofuran and uric acid) upon direct excitation of oxygen by IR laser radiation and on analysis of the action spectra of the photooxygenation reactions. Using this method, we have shown that singlet oxygen is readily formed upon laser excitation of the oxygen absorption bands at 765, 1073 and 1273 nm. The obtained data allowed for estimation of the absorption spectra, optical densities \((A_{tot})\) and molar absorption coefficients \((\epsilon)\) corresponding to the maxima of these bands in air-saturated organic solvents, water and aqueous detergent dispersions. The relative intensities of the oxygen absorption bands were shown to be markedly different from the data obtained at high pressure. Especially strong difference was found in the intensity of the 1073 nm band. In monomeric oxygen molecules (monomols), this band was shown to be 50 times weaker than in dimols \((O_2)_2\).

Fig. 1. The relative intensities of the absorption bands of molecular oxygen dissolved in air-saturated solvents (carbon tetrachloride and aqueous suspension of detergent) at normal atmospheric pressure. Results of application of laser photochemistry [9].

This conclusion correlates with the spectrum of photosensitized luminescence of singlet oxygen dimols and monomols. The molar absorption coefficients for the oxygen bands at 1273 and 765 nm were found to correlate with the \(^1\)O₂ radiative rate constants \((k_r)\) obtained from measurement of photosensitized phosphorescence of singlet oxygen.
Table 1. The most recent data of the optical densities \( A \) and molar absorption coefficients \( \varepsilon \) of oxygen molecules in air-saturated solvents estimated from the photochemical measurements (see refs below).

<table>
<thead>
<tr>
<th>Solvents</th>
<th>CCl₄</th>
<th>Acetone</th>
<th>Ethanol</th>
<th>Water + 0.2 M SDS</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_{1273} \times 10^5 ) (1 cm)</td>
<td>1.2</td>
<td>0.6</td>
<td>0.4</td>
<td>0.037</td>
</tr>
<tr>
<td>( \varepsilon_{1273} \times 10^3 ) M(^{-1}) cm(^{-1})</td>
<td>4.6</td>
<td>2.5</td>
<td>2.5</td>
<td>1.3</td>
</tr>
<tr>
<td>( A_{765} \times 10^5 ) (1 cm)</td>
<td>0.4</td>
<td>0.27</td>
<td>0.21</td>
<td>0.038</td>
</tr>
<tr>
<td>( \varepsilon_{765} \times 10^3 ) M(^{-1}) cm(^{-1})</td>
<td>1.2</td>
<td>1.2</td>
<td>1.3</td>
<td>1.3</td>
</tr>
</tbody>
</table>

It was demonstrated that in alcohol and aqueous systems, vibrations of OH groups do not sensitize singlet oxygen formation. In aqueous detergent dispersions, singlet oxygen has higher affinity to the hydrophobic micelles than to water. Within the error limit, \( \varepsilon \) of the oxygen bands did not depend upon charge of the detergent micelles. Significance of the obtained results for biomedical research and laser therapy of tumors will be discussed.

References:
The skin cancer is one of the most worldwide spread tumors and despite of the results achieved in all clinical diagnostic techniques the most severe tumor - cutaneous melanoma continues to be an important problem of social health. The limitations of standard endoscopy for detection and evaluation of cancerous changes in gastrointestinal tract are significant challenge and initiative development of new diagnostic modalities. Nevertheless if we are interested in early and precise diagnosis of skin or mucosa tumors, we need to apply appropriate and high-sensitive technique for the differentiation of tumor areas vs. normal tissue. Many optical techniques are applied recently in clinical practice for obtaining qualitatively and quantitatively new data from cutaneous neoplasia. Due to their high sensitivity in detection of small changes, spectroscopy techniques are widely used for detection of early changes in biological tissues. One of the most promising approaches is fluorescence detection of normal and abnormal tissues using naturally existing fluorescent molecules or added fluorescent markers. Fluorescent markers are applied, where native fluorescence is not informative enough to be used for diagnostic goals due to its absence, or non-specific changes in tumour vs. normal tissues. In this report we will discuss clinical applications of both diagnostic spectral modalities.

1. Introduction

Biomedical optics is one of the fastest growing areas of research. The non-ionizing nature of light applied for investigation and detection of abnormalities in human tissues make this area very attractive for development of new diagnostic techniques and modalities [1]. The optical spectra provide biochemical and morphological information about the tissue under investigation based on its absorption, reflectance, fluorescence and elastic scattering properties [1, 2]. In the last few decades fluorescence spectroscopy of human tissues becomes a matter of growing interest from the side of scientists and clinicians. Promises of this method for rapid, non-invasive, highly-sensitive detection of tissue changes allow to detect morphological and biochemical changes occurred in early stages of pathology development [1-3]. Fluorescence spectroscopy of human tissues is based on detection of emission of internal (endogenous) fluorescent compounds, as well as on application of exogenous fluorescent markers, such as porphyrins and phthalocyanines [3]. Both modalities have their advantages and disadvantages, related to their applicability in clinical practice, as well as they both are applied for investigation of skin tissue investigations. Tissue autofluorescence, where signal from naturally occurred fluorophores is detected is absolutely non-invasive and extremely sensitive technique, which theoretically could detect single tumor cell, appeared in this tissue. Problems related to its applicability are due to not enough sensitivity of the detectors applied and appearance of superposition of fluorescent signals from variety of compounds in the tissue under investigation. Autofluorescence spectra are observed mainly in blue-green spectral region for the most of the human tissues. The overlapping of the absorption and emission spectra of the most of diagnostically important compounds leads to slight differences in the observed fluorescence spectra for different pathological conditions and variations from patient to patient, due to significant dependence from the anatomic area investigated, general health status, ages, sex, even from the light sources and detectors applied [1-5]. For highly pigmented pathologies autofluorescence spectroscopy has low specificity and suboptimal diagnostic value [6]. This diagnostic modality is extremely sensitive on early changes of the tissues and if proper differentiation algorithms are applied, significant diagnostic information could be extracted from the spectra detected [1-6]. However, in some cases autofluorescence could not separate easily normal from abnormal tissue, or its benign from malignant forms, or autofluorescence intensity is too low to be used for proper differentiation. In this case exogenous fluorescent markers are applied. Third case, when exogenous fluorescent markers is applicable is when photodynamic therapy (PDT) of the tumor is foreseen to be applied for treatment of the patient. Compounds used in PDT applications have fluorescence spectra mainly in red and near-infrared spectral area and their signal could be used for diagnostic purposes [7]. Moreover, such photosensitizers have emission in the region, where endogenous fluorescence does not appear and the fluorescent contrast achieved between normal tissue and tumor is significantly higher [8].

2. Materials and methods

Investigations presented are a part of a clinical trial for introduction of spectroscopic diagnostic system for optical biopsy of skin and mucosa tumors in the common clinical practice of University Hospital “Queen Giovanna - ISUL”- Sofia. For fluorescence measurements of skin pathologies multiple wavelength excitation of the endogenous and exogenous fluorescence of benign and malignant cutaneous lesions is applied. Initially, lesions are classified visually by experienced dermatologist and dermatoscopically using ABCD scoring criteria. Second step is detection of lesion and surrounding normal skin autofluorescence using different excitation wavelengths, namely 365, 385, 405 nm and 630
nm, received from several narrow-band light-emitting diodes. Optical fiber probe is used to deliver the light from LEDs and to collect the fluorescence signals from the skin surface. It consists of 7 fibers in circular geometry. Central fiber is used for autofluorescence signal detection and it is connected to microspectrometric system and surrounding six fibers are used for delivery of excitation light from the LEDs to the skin under investigation.

For fluorescence measurements of gastrointestinal pathologies excitation sources at 405, 530 and 630 nm are applied. Optical fiber probe, consisting of 6 emitting fibers and one collecting fiber, is applied through instrumental channel of the endoscope for detection of tumors in esophagus and stomach.

For both kind of tissues and all pathologies investigated, as exogenous fluorescent marker is used Protoporphyrin IX. Initially 5-ALA is applied topically, as a cream for the skin lesions and orally – as a water solution (20 mg/kg dose) for the gastrointestinal lesions. After 6 hours exogenous fluorescence detection of accumulated in the pathologies protoporphyrin IX was carried out.

Both kinds of spectra – autofluorescence signals and protoporphyrin IX signal are recorded and stored using a fiber-optic microspectrometer (USB4000, Ocean Optics, Dunedin, FL, USA). A personal computer is used to control the system and to display the data using the specialized microspectrometer software OOI Base (“Ocean Optics”, Inc., Dunedin, FL, USA). Normal tissue fluorescence was both localizations as a basis for comparison with the pathologies observed.

3. Results and discussion

Normal tissue autofluorescence spectrum, when excitation in the end of UV and blue spectral range is applied, consists mainly from fluorescence signals of collagen, elastin, protein cross-links, NADH and flavins [3-5, 7]. The autofluorescence spectra observed are distorted from the re-absorption of melanin in case of skin lesions and different forms of hemoglobin for skin and mucosa lesions respectively.

In the case of most common cutaneous tumor – basal cell carcinoma (BCC) autofluorescence could be applied as a diagnostic tool. Usually the spectra obtained from BCC lesions have not significant spectral shape changes vs. normal skin spectra, but are with lower intensity, which allow to reach sensible diagnostic accuracy. Advanced stages of BCC lesions reveal red fluorescence, which appear due to endogenous porphyrins, accumulated in the tumor areas [9]. To increase the diagnostic accuracy and to develop user friendly technique for 2-D fluorescence imaging of skin BCC lesions exogenous 5-ALA/PpIX was applied. Fluorescence imaging has been shown to be a potential complement to visual inspection for demarcation of basal cell carcinoma lesions [10].

In the case of esophageal and stomach tumors the autofluorescence spectra of the lesion area are not significantly different by shape and intensity from the surrounding normal mucosa. Some additional absorption of hemoglobin is observed in lesion’ areas, but false-positive results in this case are observed when inflammatory tissues have place as well. Autofluorescence results gives high sensitivity (>90%), but extremely low specificity (~55-60%), which is not acceptable for a technique, which must improve the diagnostic accuracy of initial tumor detection and evaluation of tumor borders and spreading lesions in the mucosa investigated [11]. These drawbacks are overloaded when exogenous fluorophore 5-ALA/PpIX is applied. Sensitivity and specificity observed for both localizations – esophageal and stomach carcinoma lesions exceed 90%, which make the exogenous fluorescence diagnosis of gastrointestinal tumors and useful tool for clinical practice.

4. Acknowledgements

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References

LASER-ASSISTED MICROSCOPY FOR TUMOR CELL RECOGNITION

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Methods of laser assisted microscopy for tumor cell recognition – including fluorescence, elastic and inelastic light scattering - are summarized. Differences between tumor cells and less malignant cells are based on their emission spectra, fluorescence lifetimes and cell-substrate contacts. Raman spectra as well as the angular dependence of elastic scattering may be used for further discrimination. In addition, differences in 3-dimensional cell growth should be considered.

1. Introduction
Methods of label-free diagnostics – including fluorescence, elastic and inelastic light scattering – appear promising to distinguish tumor cells from less malignant cells or tissues. Therefore, as a test system for a comparison, isogenic cell lines from human glioblastoma were used prior and subsequent to activation of tumor suppressor genes. Fluorescence spectra, lifetimes, cell-substrate contacts and Raman spectra were evaluated, and 3-dimensional cell growth as well as the angular dependence of elastic scattering were further considered.

2. Materials and Methods
Genetically engineered U251-MG glioblastoma cells (kindly supplied by Prof. Jan Mollenhauer, Dept. of Molecular Oncology, University of South Denmark, Odense) were used with the tumor suppressor genes TP53 or PTEN being over-expressed, such that these cells exhibited a reduced tumorigenic potential and may be regarded as less malignant. Highly malignant U251-MG cells without suppressor gene served as controls. In addition, MCF-7 breast cancer cells (malignant controls and cells transfected with the pro-oncogene c-myc) were used.

Wide-field fluorescence and Raman microscopy was used in combination with spectral imaging, fluorescence lifetime imaging and multivariate statistical methods. In addition, cell-substrate topology was examined by variable-angle Total Internal Reflection Fluorescence Microscopy (TIRFM). 3-dimensional cell growth was observed by structured illumination, while angular dependence of light scattering was measured with a modified microscope permitting a defined angle of laser illumination.

3. Results and Discussion
Upon excitation in the near ultraviolet range (375 nm) U251-MG tumor cells and less malignant cells were distinguished by the ratio of fluorescence intensities measured around 440–450 nm and 470–490 nm and mainly attributed to the ratio of the protein-bound and free coenzyme NADH [1]. This result was further supported by slight differences of fluorescence lifetimes and discussed in the context of a different cell metabolism. Cell-substrate distances of tumor cells (growing on a glass slide) were rather constant (around 100 nm), but varied strongly between only a few nanometres and up to 300 nm for the less malignant cells, thus revealing that focal contacts and larger distances were in close vicinity. Raman spectra showed slight differences between malignant and less malignant cells around 970 cm⁻¹, mainly originating from granules surrounding the cell nucleus.

3-dimensional growth of all glioblastoma cell lines resulted in multicellular spheroids of up to 500 μm diameter, but differed between MCF-7 breast cancer cells and MCF-7 cells transfected with the pro-oncogen c-myc. Here, typical spheroid sizes were about 300 μm in the first and 120 μm in the second case.

Reference
Development of new PDT method based on genetically encoded photosensitizer

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In this study we have demonstrated for the first time that phototoxic fluorescent protein KillerRed can be successfully used to damage gene-transfected HeLa cancer cells in vitro and in vivo. Histological data have shown that laser irradiation of KillerRed expressing tumors in mice led to substantial dystrophic cellular changes such as disruption of cellular and nuclear membranes, nuclei swelling, and activation of apoptosis. The results suggest KillerRed as a potential genetically encoded photosensitizer for photodynamic therapy (PDT) of cancer (if efficient technologies of gene delivery to tumors are developed).

1. Introduction

Recently it was discovered that a red fluorescent protein named KillerRed showed pronounced phototoxic properties [1]. By now it has been demonstrated that KillerRed can be successfully used for phototoxicity-based optogenetic manipulations. In particular, it has been applied in vivo to observe the role of reactive oxygen species in transgenic zebrafish [3] and affect cell division in Xenopus embryos [2]. KillerRed is also suitable for chromophore assisted light inactivation (CALI) of target proteins, which has been shown by the examples of β-galactosidase, pleckstrin homology domain of phospholipase C (PLCδ1), β1A integrin and RNA-binding motif protein encoded on the X chromosome (RBMX) [1, 4, 5]. Other promising application of the protein is a precise light-induced killing of the target cell populations. The phototoxicity of KillerRed has been found to depend greatly on its intracellular localization. In cytoplasm, this protein has shown a very low phototoxicity. At the same time, mitochondrially localized KillerRed (KillerRed-Mito) has caused an efficient light-induced caspase-mediated apoptosis [1]. KillerRed directed to the plasma membrane also has shown a high phototoxicity [6]. Finally, mammalian cells expressing a fusion of core histone H2B with tandem KillerRed (H2B+tKR) have demonstrated very efficient light dependent blockage of the cell divisions due to genomic DNA damage [2].

2. Materials and methods

The strongly adherent HeLa Kyoto cell line was used. HeLa Kyoto cells were cultured in DMEM supplemented with 10% FBS (Hyclone), 2 mM glutamine (PanEco), 10 U/ml penicillin and 10 µg/ml streptomycin. Cell cultures stably expressing H2B-tKR and KillerRed-mito constructs were obtained by lentiviral transduction.

Female athymic nude mice, 4 weeks old, weighing 18–20 g were used. The s.c. tumors were induced by injecting 5x10⁶ HeLa cells suspended in 0.1 mL PBS into the mouse flank. Tumor growth was documented regularly by external measurements with calipers. A total of 16 mice were randomly divided into four groups of four animals (two treated and two untreated control with and without KillerRed correspondingly). All in vivo experiments were done in accordance with the guidelines approved by the Ethical Committee of the Nizhny Novgorod State Medical Academy. A diode pumped solid state yellow laser (MGL, Changchun New Industries Optoelectronics Tech. Co., Ltd. (CNI) P.R.China) with 593 nm wavelength was used throughout this study. The light was delivered through an optical fiber and irradiated the tumor surface over a 6 mm-diameter beam spot. During the irradiation tumor temperature was measured from the surface by IR thermograph (CEM®-ThermoDiagnostics, CEM-Technology, Russia). 24 hours after the last light treatment, tumors were excised, sectioned, and stained for light and electron microscopy.

Whole-body in vivo fluorescence imaging was performed with a home-built back-reflectance imaging system (Institute of Applied Physics RAS, Russia). The system is equipped with LED at the wavelength of 585 nm to excite the fluorescence. A high sensitive cooled CCD camera Hamamatsu ORCAII-BT-512 and an emission band-pass filter were used to detect the fluorescence in the 645-730 nm range. All fluorescence images were acquired with 5-second exposure time. Serial brightfield photographs and fluorescence images were acquired before and at multiple time points after laser treatment.

For histological examination, 24 h after the last treatment tumors were surgically removed and fixed in 10% neutral-buffered formalin, dehydrated and embedded in paraffin. Four micrometer sections were stained with hematoxylin and eosin (H&E) and Feulgen stains and examined with light microscopy. The cancer cells in H&E stained slides of each tumor were counted in 8-18 randomly selected microscope fields of 0.01 mm² at 400x magnification. Percentage of the typical (unaltered) cells, altered cells, and mitotic figures was measured.
3. Results

HeLa Kyoto cells were co-transduced with two lentiviruses encoding KillerRed-Mito and H2B-tKR. The resulting cell line (HeLa Kyoto KillerRed-MitoH2B) demonstrated stable expression of both, KillerRed-Mito and H2B-tKR and the corresponding red fluorescence in mitochondria and nuclei. It was noticed that the fluorescence intensity in the KillerRed-expressing tumors dropped immediately after the laser irradiation, which indicated photobleaching of the fluorescent protein (Fig. 2). This result supports the idea that KillerRed is activated in tumors in vivo similarly to the in vitro assays. It was found that after the irradiation fluorescence of KillerRed in tumors was less than that before the procedure by 31.6±9.4%.

Histological examination showed that untreated non-expressing KillerRed HeLa tumors had a compact dense tissue structure and consisted of large polymorphic cells tightly packed together. The tumors were poorly vascularized. The cells had large round or oval nuclei containing fine dispersed chromatin. Lightly basophilic cytoplasm gathered around the nucleus as a thin ring. The tumor cells formed complexes surrounded by thin layers of the connective tissue with thin-walled small blood vessels. The typical (without any morphological changes) cancer cells amounted to 84.3% of the total number of cancer cells in the field of view. To evaluate the nuclear condition histological sections were stained with Schiff reagent specific for DNA (Feulgen stain). In the Feulgen-stained slides high chromatin content was observed, and distribution of the chromatin in most nuclei was uniform.

No significant difference in the tissue structure between KillerRed-expressing and non-expressing HeLa tumors was observed. Quantitative data were close to those of the untreated HeLa tumors without KillerRed. Feulgen staining revealed slightly higher nuclei polymorphism, which appeared in their irregular shape, increase or decrease in size, as well as decrease of nuclear Feulgen-positive material.

In the treated tumors without KillerRed a slight increase in the proportion of dystrophically changed cells (up to 18.8%) was found. The cell structure aberration observed was mainly cytoplasm vacuolization in some cells. In Feulgen-stained slides no changes in the tissue structure between KillerRed-expressing and non-expressing HeLa tumors was observed. In contrast, extensive morphological changes were observable in the treated tumors expressing KillerRed in nuclei and mitochondria. Most cells had strongly vacuolated cytoplasm, to the extent of plasma membrane destruction in some cells. In a fraction of the treated cells nuclei, round or irregular, were enlarged due to swelling, and their carioloema was broken. The percentage of dystrophically changed cells increased to 63.7%. Abnormalities indicating apoptotic cell death occurred in 14% of the cells. The portion of unaltered cancer cells went down to 21.1%. Mitotic activity also showed a weak tendency to decrease. Feulgen's nuclear reaction revealed a significant change of nuclear structure in the tumor cells. A strong alteration of chromatin distribution was observed, as indicated by drastic decrease or loss of Feulgen-positive DNA.

References

Abstract - In this work we characterize the properties of the laser-induced air plasma as a detector of THz radiation. Special attention is drawn to the question of linearity of its response and possibility of calibration. A new way to extract the absolute value of THz pulse electric field using a time-domain measurement system is presented.

It is generally accepted that laser-induced breakdown air plasma may be successfully utilized for generation of terahertz radiation. In extreme case THz spectral range within this approach is determined only by the optical pump pulse duration therefore resulting in a broadband THz signal spectrum. Besides, laser plasma can be efficiently used for the purpose of coherent detection of THz radiation (so-called ABCD technique) [1], [2]. In that case plasma-based detector can be regarded as a matched one for plasma-based THz emitter as far as the conformity of their frequency bands is concerned. Therefore implementation of the emitter-detector system, with both of those based on laser spark plasma, seems promising to applications due to unprecedented wideness of the covered spectral range.

This work presents a study of the ABCD technique, focusing mainly on the nuances of its application to spectroscopic measurements. Among the most important points here are: linearity of the detector response and the possibility of its calibration.

An ABCD detection is a classical correlation scheme that utilizes the third order non-linear susceptibility of the medium [1]. The correlation is measured between the pulse of THz radiation and optical fundamental frequency pulse (detection pulse), that is a direct replica of the one used for corresponding THz pulse generation (generation pulse). The scheme consists of a pair of plain high-voltage electrodes, arranged in the vicinity (see fig. 1) of the focal plane of the lens that is guiding the detection beam into the scheme. The third order non-linear process, taking place in the area between electrodes results in generation of the second harmonic of the fundamental frequency radiation which then can be detected directly. Applying a meander-like voltage signal to the electrodes, one can achieve a heterodyne (i.e. it is possible to extract THz pulse spectral amplitude and phase simultaneously) mode of the ABCD setup operation if the meander frequency equals half of the laser repetition rate.

Linearity of the ABCD detection scheme upon THz pulse electrical field amplitude was tested using a calibrated optoacoustic integral detector (a Golay cell), placed in the THz beam path. Data acquired by the Golay cell was compared with the time-integrated profile of the THz pulse electrical field, recorded using a time-domain (TDS) ABCD measurement. A good correlation of these can be seen from fig. 1:

Figure 1: Schematic representation of an ABCD detection scheme.

Figure 2: Comparison between time-integrated TDS data, acquired by the ABCD scheme and Golay cell readings.
The square-like law depicted by fig. 1 is related to the fact that THz beam power can not be varied directly; instead, we vary the power of the optical radiation used for the generation of THz emission. Since the generation process is non-linear itself such dependence of emitted (and hence detected) THz power on input optical energy is observed.

Due to the nature of the ABCD technique as a heterodyne method, it is possible to determine absolute value of the measured THz pulse electric field. This can be achieved simply by comparing the level of the detected signal (in arbitrary units) given, for example, by a lock-in amplifier in cases of presence \( S \) and absence \( S' \) of THz radiation entering the detection scheme. Since the bias voltage \( E_{DC} \), applied to the area of THz radiation detection, is known and can be regarded taking part in the non-linear process as an equal to THz field:

\[
E_{2\omega} \propto \chi^{(3)} E_\omega E_\omega (E_{DC} + E_{THz})
\]

We conclude (after some math) that:

\[
E_{THz} = E_{DC} \left( \frac{S}{S'} - 1 \right)
\]

We have calculated the amplitude of the THz pulse field \( E_{THz} \) for different values of the applied bias voltage (fig. 3); for our set of experimental conditions (“bichromatic” scheme of THz emission excitation; 500 \( \mu \)J per 120fs fundamental pulse in the generation arm at 800 nm, 15 cm lens focal distance) \( E_{THz} \) is evaluated as 1 kV/cm with almost no dependence on the bias field value. It is also worth noting that the THz field pulse amplitude, estimated from Golay cell experimental data, also made up a value of 1 kV/cm, with a difference of about 100 volts in relation to the ABCD calibration method presented above.

Figure 3: Detected second harmonic signal for the cases of blocked and open THz beam paths. Curves are approximated by a quadratic law to show that the detected signal is proportional to the THz or bias field amplitude to the power of two.

Summarizing, we conclude that the so-called Air-Biased Coherent Detection (ABCD) technique can be considered fairly linear within the studied range of THz pulse amplitudes (up to 1 kV/cm and even higher). Therefore this method can reliably be applied to broadband THz time-domain spectroscopy. In addition, we suggest a new way of absolute value of THz pulse field estimation. Using this method one can easily estimate THz field amplitude for any source without usage of any additional equipment. The only requirement for this technique is that the whole THz generation and detection setup is built in a time-domain measurement allowing form (i.e. includes a delay line).

References
THZ AND RAMAN SPECTROSCOPY IN STEROID CHEMISTRY

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The terahertz time-domain and Raman spectra of steroids in the region of 0.1-3.0 THz have been measured. Steroids have several intense and specific absorption features in the THz frequency region. The features are uniquely determined by a hormone structure. This allows us to analyze steroids in complex samples such as pharmaceuticals, foodstuffs and biological fluids, and in process of the pharmacological and chemical synthesis.

1. Introduction

Steroids are the organic compounds that contain a characteristic arrangement of four cycloalkane rings that are joined to each other. Examples of steroids include the dietary fat cholesterol, the sex hormones estradiol and testosterone, the anti-inflammatory medicines dexamethasone and acetate cortisone. The core of steroids is composed of twenty carbon atoms bonded together that take the form of four fused rings: three cyclohexane rings (designated as rings A, B, and C in the Fig.1) and one cyclopentane ring (the D ring).

Figure 1: The basic skeleton of a steroid. R1, R2, R3 and R4 can be methyl group, and X - hydroxyl or keto group.

The steroids differ only by the position of functional groups attached to this four-ring core and by the oxidation state of the rings. The biological action of steroids is closely related to some features of their chemical structure. The steroids are aggregated into the molecular crystals of two space groups P2₁2₁2₁ and P2₁, in general. The molecules could be bound by van der Waals and/or stronger hydrogen forces in molecular crystals. Thus, steroids are convenient object for study of a nature of low-frequency vibrations and affects of hydrogen bonds.

The steroid hormones influence on many physiological processes in humans and animals is well known. Their crucial role in regulating life processes led to a widespread research in steroid chemistry and biochemistry, creating new and fast methods of steroid analysis in biological samples, as well as in food, sewage and pharmaceutical production. Steroids have rather complex molecular structure, show significant reactivity with similar physico-chemical properties and are often located in low quantities in multicomponent matrices. The determination of steroids and their metabolites in biological samples and pharmaceutical drugs can be done by chromatography, mass spectrometry, ELISA and other methods of analysis with high accuracy. However, these methods are time consuming and expensive. In this regard, the development of new operational methods of analysis is highly relevant. The methods of THz-TDS spectroscopy can be helpful for the study of steroids. This type of spectroscopy has a number of advantages such as the possibility to analyze a wide frequency band in a single measurement, to obtain time resolution and phase information, and to measure the complex dielectric permittivity which completely characterizes the optical response of the matter. At the same time, THz-TDS is able to penetrate many opaque materials, but unlike X-rays, it is non-ionizing radiation and can detect the samples without influence or destroys. Moreover, THz spectra of molecular crystals show rich information about collective vibrations and are highly sensitive to the changes of the molecular conformation, structure, environment elements and intermolecular interaction than IR spectra. The aim of our research is to study a wide range of steroids by THz-TDS and Raman spectroscopy.

2. Materials and methods

Steroids were purchased from Koch-Light Laboratories Ltd, UK, and were used without further purification. For THz-TDS measurements the samples were prepared by pressing the pure polycrystalline powder to disks of thickness 0.4 mm, diameter 5 mm and average density 1.2 mg/mm³ by applying a pressure about 50 MPa. For the case of thin films and solutions we developed total internal reflection (TIR) scheme using silicon right angle Dowe prism [1]. The description of the THz-TDS apparatus was given in [2]. The Raman spectra were recorded as in [3].

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3. Results

We studied different classes of steroids: corticosteroids, androgen and estrogen, and related medicine. Spectral properties of steroids are well described in UV and IR spectral range, but those spectra are similar. Only in THz region substances have several intensive unique features.

Figure 2: The THz absorption spectra of acetate: corticosterone (1), deoxycorticosterone (2), cortisone (3) and hydrocortisone (4). The spectra are shifted along the vertical axis.

The steroid acetate room temperature THz absorption spectra are shown on Figure 2. The substances have several intense spectral features in the frequency range 0.1-3.0 THz. The features are uniquely determined by a hormone structure. This allows one to analyze a complex mixture on specific frequencies and to obtain information about individual components.

Thus, THz-TDS can be used to analyze steroids in complex samples such as pharmaceuticals and in process of the pharmacological and chemical synthesis.

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References


Efficient femtosecond optical parametric amplification and wavelength conversion in silicon waveguides

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Abstract: Efficient femtosecond parametric amplification and wavelength conversion via four-wave mixing in silicon waveguides are demonstrated. The flat quasi-phase-matching, smooth temporal profiles and separable spectra for 200 fs pulses are obtained by tailoring the cross-section of the rib silicon waveguide. On-chip parametric gain as high as 26.8 dB and idler conversion gain of 25.6 dB is achieved with a low pump peak power over a flat bandwidth of 400 nm in a 10-mm-long dispersion engineered silicon waveguide. The conversion bandwidth of 220 nm with peak conversion efficiency of -8 dB is demonstrated using 500 fs pump pulses.

Silicon-based optical devices with micro-nano structures can offer a variety of nonlinear effects that can be used to process optical signals at the high speed of 100 Gbit/s and beyond, detect signals at unprecedented sensitivities for novel sensing applications and enable broadband electro-optic modulation. In recent years, the nonlinear silicon photonics has attracted a great deal of attention because of its potentially lower cost and high compatibility with CMOS industry, which is interested in combining new optical functionalities with electronics on a single chip. Compared with the conventional high nonlinear optical fibers, the silicon waveguides have inherent advantages due to the large values of Kerr parameter and Raman gain coefficient, the flexible dispersion engineering and the tight confinement of optical mode [1]. Parametric processes via four-wave mixing (FWM) have also been explored in silicon waveguides typically on time scales ranged from the continuous-wave to the picosecond regime. In detail, parametric gain with a 1.8 dB gain over 60 nm bandwidth has been demonstrated in silicon waveguides with picosecond pump [2]. The conversion efficiency of -8.6 dB using reverse biased p-i-n rib waveguides was obtained with continuous-wave pump [3]. On-chip optical parametric oscillator based on the silicon waveguide can generate more than 100 new wavelengths with operating powers below 50 mW [4]. Despite these progresses, there is still a strong motivation to explore femtosecond optical parametric amplification and wavelength conversion in silicon waveguides. Here we demonstrate the efficient femtosecond optical parametric amplification and wavelength conversion via FWM in silicon waveguides.

The parametric process is investigated by simultaneously injecting pump pulses and signal pulses with the same pulse width in silicon rib waveguides. The rib height (H) and the etch depth (h) are 300 nm and 260 nm, respectively. The quasi-phase-matching can be satisfied in the anomalous GVD regime. Careful choice of the waveguide width (W) is required to obtain anomalous-GVD at the pump wavelength (1550 nm), we can change the rib waveguide width to tailor the zero-dispersion wavelength (ZDWL). We choose 550 nm, 600 nm and 650 nm from the series of widths as the waveguide widths, and the GVD of the three waveguides is shown in Fig. 1. Figure 2 depicts the spectra at the input and output of the rib waveguide with 550 nm width for a 1550 nm pump with 5 W peak power and 1450 nm signal with 1 W peak power when the pump and signal pulse width are 100 fs, 300 fs, and 500 fs, respectively. It is obvious that the signal was efficiently converted and amplified into an idler at wavelength of 1665 nm. Because of self-phase modulation (SPM) and cross-phase modulation (XPM), all of the output spectra are broadened and spectral overlap appears for the 100 fs pulses as shown in Fig. 2. The spectral broadening is much larger for shorter pulses in the femtosecond regime and spectral overlap can not be avoided in this case, which are less than 100 fs. Therefore it is difficult to achieve a wavelength converter and amplification when the input pump and signal pulse widths are close or less than 100 fs.

The lengths of the three waveguides are 10 mm and the input pump peak power is 5 W, while the signal peak power is 1 mW in the process of OPA. The repetition rate of pump and signal pulses is 0.1 GHz, which means low free carrier effects for femtosecond pulses. The spectrum of pump is greatly broadened when the width of the waveguide is 550 nm, covering the signal and idler spectra as shown in Fig. 3 (a). With increasing the width of the waveguide, the degree of spectral broadening is decreasing. Fig. 3 (c) shows the signal and idler spectra only have little overlap with the pump spectrum. Therefore, separable spectra can be achieved by tailoring the dispersion profiles of the silicon waveguide. The OPA with an on-chip parametric signal gain of 26.8 dB and idler conversion gain of 25.6 dB over a flat bandwidth of 400 nm is achieved as shown in Fig. 4.
At the same time, the initial chirp can lead to drastic changes in the pulse spectrum. Figure 5 shows the spectra at the output of the rib waveguide with width of 650 nm for a 1550 nm pump and 1450 nm signal with different initial chirps. Both of the pulse widths of the input pump and signal are 200 fs with peak power of 6 W and 1 W, respectively. Separable FWM spectra with most of the energy remains in the central peak can be obtained by optimizing the initial chirp. In this case, the optimal chirp is a range from -1 to -2 as shown in Fig. 5. Figure 6 (a) shows the FWM spectra with signal tuned from 1350 to 1500 nm. The repetition rate of pump and signal pulses is 40 GHz with initial chirp C=-2. Therefore, efficient wavelength conversion can be achieved using this rib waveguide with flat bandwidth over 500 nm. The conversion efficiency is shown in Fig. 6 (b), and conversion efficiency as high as -1.6 dB is obtained.

In conclusion, we have demonstrated efficient femtosecond parametric amplification and wavelength conversion via degenerate FWM in silicon rib waveguides. The influences of spectral broadening, dispersion profiles and initial chirp on the parametric process are investigated. The spectral overlap can be suppressed by tailoring the dispersion profiles of the silicon waveguides, and separable spectra are obtained for parametric amplification with 200 fs pulses. The on-chip parametric gain as high as 26.8 dB over a flat bandwidth of 400 nm are obtained for a pump peak power of 10 W in a dispersion engineered silicon waveguide.

References

Rapid fabrication of the micro-lens array by holographic lithography is presented. The holographic lithography enables fabricating the micro-lens array with a good focusing ability by a single laser exposure over a large area (more than 5x5 mm). The focal length of fabricated micro-lenses can be controlled by manipulating the laser fabrication parameters such as the average laser power, repetition rate or exposure time. The fabricated micro-lenses can be used for various practical applications: fiber coupling and optical switching, collimation of laser diodes, imaging systems and sensors, beam homogenizers for lasers and illumination systems.

Holographic lithography (HL) [1, 2] is a powerful technique which allows fabrication of periodic microstructures over a large area. This technique is based on the recording of the interference pattern into a photosensitive material. The HL technique enables fabricating 2D and 3D periodic structures over large areas by a single laser exposure. The certain advantage of HL is the rapid fabrication of periodic structures. By using this technique rapid manufacturing of different periodic structures such as pillars and micro-tube arrays with different periods or more complex periodic microstructures such as photonic crystals or C-shape structures is possible. The shape of fabricated periodic microstructures depends on phase, polarization and the number of used laser beams. The period of produced periodic structures can be controlled by wavelength of the used laser and angle between interfering beams. The theoretical smallest period which can be fabricated by HL is equal half of the used laser wavelength (diffraction limit).

In this presentation we demonstrate the possibility to fabricate the micro-lens array by using the holographic lithography technique. Micro-lenses were fabricated using an experimental setup which consisted of a femtosecond Yb:KGW laser (Pharos, Light Conversion, Ltd.) generating ~250 fs pulses at 515 nm (second harmonics) with the tunable repetition rate from 1 to 600 kHz, a beam expander which reduced the diameter of the initial laser beam by 3 times, a diffractive optical element (DOE) with 2 deg separation angle between beams and a grating period of 30 μm (MS0203, HoloOr Ltd.) which splitted the laser beam into four identical beams, diaphragm (D) which blocked undesirable higher order diffracted beams and two lenses (L1 and L2) with the focal length of 25 mm and 150 mm, respectively, which collected four beams into the sample (Fig. 1).

In experiments a commercial hybrid organic-inorganic Zr-containing negative photoresist SZ2080 (chemical formula C₄H₁₂SiZrO₂) [3] (FORTH, Greece) with 2% by w.t. concentration of photoinitiator 4,4'-bis(dimethylamino)-benzophenone was used.

A theoretically calculated micro-lens array profile in the four beam interference case is shown in Fig. 2 c). The intensity distribution and wave vectors of four interfering beam which were used in calculations are depicted in Fig. 2 b) and a),
respectively. Theoretical evaluation shows that the shape of micro-lenses becomes parabolic and depends on the intensity distribution.

![Figure 2: a) the wave vectors of interfering four beams. xyz denotes coordinate system, \( k_1, k_2, k_3 \) and \( k_4 \) are the wave vectors of the interfering beams, \( \theta \) is the angle between the beam and \( z \) direction. b) the intensity distribution for the interference field of symmetrically arranged laser beams, \( xy \) denotes coordinate system, \( I \) is the intensity distribution in the interference pattern. c) the theoretically calculated micro-lens array profile.](image)

The example of fabricated micro-lens array is shown in Fig. 3 a). The fabricated micro-lenses demonstrate the focusing ability and the possibility of imaging objects (Fig. 3 b). In Fig. 3 b) the image of the CPST logo pattern taken by the lenses manufactured by HL technique is shown. The focus length of manufactured micro-lenses can be controlled by manipulating the laser irradiation dose during the lenses fabrication process. The focal length of micro-lenses in Fig. 3 was about 200 µm. The processing area by a single laser exposure was more than 5 mm x 5 mm and it means that the fabrication of the micro-lens array can take only several minutes. During to this feature, the fabrication process of the micro-lens array by the HL technique becomes very attractive and promising.

![Figure 3: a) micro-lens array fabricated by holographic lithography technique. Process parameters: laser wavelength – 515 nm, average laser power ~ 530 mW, repetition rate – 10 kHz, exposure time ~ 5 min. b) Image of the CPST logo pattern taken by the lenses is shown in a).](image)

References
This work presents the use of the Laser Induced Forward Transfer (LIFT) process as an advanced tool for biosensors and chemical sensors fabrication. LIFT is an alternative micro patterning technology that employs pulsed laser irradiation for the selective deposition of a liquid or solid target material including organic, carbon based nanomaterials, biological compounds, metal nanoparticles, and dielectrics at different kind of substrates including flexible materials. More specifically, LIFT process is used for direct printing of biomaterials (enzymes and photosynthetic proteins) for environmental biosensors fabrication. The use of LIFT revealed the possibility of direct immobilization of the biomaterials onto the surface of the sensors without the use of chemical linkers. The laser printed droplets induce high impact pressure on the sensor surface, which is calculated a few MPa. This pressure is higher to the barrier required to transit from a partial to a complete wetting state. As a result of this wetting state transition the physical adsorption of the biomaterial on the electrodes surface is enhanced. Those observations are of significant importance for the robustness characterization of super-hydrophobic surfaces under the extremely high liquid impact, which is achieved by LIFT.
EFFICIENT NONLINEAR-OPTICAL REFRACTION AND ALL-OPTICAL SWITCHING IN MESOPOROUS SILICON BASED STRUCTURES

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Up to four-order enhancement of the nonlinear optical cubic susceptibility in mesoporous silicon films compared to crystalline silicon was found under its irradiation at wavelength of 1064 nm by picosecond laser pulses. These efficient nonlinear-optical responses can be attributed to the resonant excitation of the defect states in the band gap of silicon and local-field enhancement in the mesoporous films. The microcavity resonance shift up to 10 nm in a mesoporous silicon based photonic crystal microcavity was revealed at intense laser excitation. So the fast all-optical switching was realized owing to the strong nonlinear-optical refraction and free carrier generation processes.

1. Introduction
Silicon-based nanocomposites are very promising materials for the light control and nonlinear optics. The porous silicon formed by silicon nanocrystals separated with voids (pores) is a good sample of this nanocomposite attracting a great deal of interest. Relatively high cubic susceptibility of silicon combined with well-developed surface and local field effects result in significant enhancement of the nonlinear-optical interaction efficiency in this material [1-3]. The mesoporous silicon films with the pores ranging from 10 to 100 nm allow us to study the mentioned effects. In this work the light self-action and all-optical switching in mesoporous silicon layers and photonic crystals microcavities were studied respectively.

2. Results and discussion
The anisotropic mesoporous silicon structures were produced by the electrochemical etching method using the highly doped monocrystalline Si wafers [2, 3]. To study the nonlinear refraction of porous silicon we employed of a mode-locked Nd:YAG laser radiation (1.064 μm, 40 ps) transmitted through the porous silicon monolayer samples. We analyzed dependences of both total and on-axis transmittance on the incident laser intensity. The obtained dependences demonstrate two regions of the incident intensities: below 4 MW/cm² and above 10 MW/cm² (see “Fig. 1” for the total transmission), caused by the resonant excitation of the restricted number of the surface states and local-field enhancement respectively in the sample volume.

Figure 1: Total transmittance of the birefringent sample in dependence on the laser intensity for samples with porosity 49% (a) and 73% (b). The crystallographic direction [001] corresponds to the optical axis. E is the electric field.
The mesoporous Si samples demonstrate efficient self-focusing in both intensity regions. The cubic susceptibility for the mesoporous silicon exceeds one for the crystalline silicon four orders of magnitude in first case and two orders of magnitude in second one.

The high nonlinear-optical refraction in the mesoporous silicon allows considering this material as a base for ultrafast optical control. We designed photonic crystals microcavities based on the mesoporous silicon and carried out pump-probe experiments with them using the picosecond Nd:YAG laser radiation and a delay line. The microcavity resonance shifts up to 10 nm at the laser intensities about 4 MW/cm² (“Fig. 2”).

The value of such shift depends on the laser pulse intensity and delay time between the pump and probe pulses. Upon a closer view were revealed that such switching have been caused by three competitive process: the Kerr nonlinear-optical refraction, free carrier generation and thermal nonlinearity at high-intensity laser fields in time scale up to tens of picoseconds.

So we demonstrate a possibility using the mesoporous silicon structures for the fast control of light via light.

References
We have recently shown that broad waveguides with Littrow diffraction at one of their boundaries produce a set of sharp resonances in a silicon-on-insulator implementation at 1550 nm. We capitalize on the fact that longer waveguides behave as multiple series resonators to investigate the cubic nonlinear triply resonant wavelength conversion process. The free-spectral-ranges of our waveguides are in the 15-25 nm range. Triply resonant conversion demands equal spacing, thus controlled dispersion, which could be achieved by playing with multiple resonators and the rest of the parametric space of these systems.

1. Introduction

Broad periodic waveguide with side corrugation can offer flat bands and slow light of multiple modes in the so-called critical coupling regime. Several novel phenomena have recently been highlighted in broad periodic waveguides: “critical coupling” and “collective slow light” [1], “Littrow lasing” [2], the experimental evidence of the “stripe of minigaps” [3]. Critical coupling occurs when the anticrossing between the “net” of multiple modes has just the right value to flatten a large region of the dispersions around the edge of the Brillouin zone [4]. Exploiting these systems for nonlinear optics is made attractive by the possibility of triple resonance. In principle, a device akin to a FP with multiple resonance can accomplish triply resonant wavelength conversion $\omega_{\text{idler}} = 2\omega_{\text{pump}} - \omega_{\text{signal}}$. But in a solid state resonator, the material dispersion is a well-known impediment to good phase matching: the FSR tends in general to diminish at higher frequencies (normal dispersion), and very high design constraints have to be included by optogeometric means (exact waveguide shape etc.) to get equalized free-spectral-range (FSR). Here, we propose that dispersion is relaxed, but that the multiple peaks in the long devices can be used to get phase matching even in the presence of substantial dispersion, which is very promising for topics such as frequency comb generation [5, 6].

2. Experiment principle and results

The broad waveguide is made of silicon-on-insulator, processed by the EpixFab facility. Schematic overview is presented on Fig.1(a). Littrow diffraction forms regular 45° triangle structures, and there is a resonance between each reflection on the grating. The order $m$ of these resonances is typically $m \sim 50$ or $m \sim 75$ at 1550 nm, depending on the designed width $w$. Each resonance acts as a Fabry-Perot (FP), so that a waveguide of some length behaves exactly as FP in series: although there is no transmission mirror and the guide looks as a defect-free periodic structure, light goes serially between the different resonating areas. Fig.1(b, top) shows a structure that supports the equivalent of three FP resonators. Results are obtained for devices of different length analogue to single-, double-, and triple-FP, different orders $m=50$ associated to ~25 nm FSR or $m=75$ associated to 15 nm FSR, and different teeth shape obtained by varying the aspect ratio height/period = $h/a$ with the constant period $a=385$ nm. This parameter dictates the coupling strength. Experimental technique and full discussion is presented in [7]. In Fig.1(b), we show transmission spectra of two devices behave similar to triple-FP resonator.

Figure 1: (a) Sketch of a typical Epixfab chip/sample; (b) in-plane layout for triple resonance (top) and it’s experimental transmission spectra with variable degree of resonance, depending on the teeth aspect ratio $h/a$ as indicated (bottom).
We see for instance that the case $h/a=4.00$ corresponds to non-flat bands, thus broader minibands and smoother peaks, whereas $h/a=3.00$ is closer to the critical coupling condition, and nice and sharp triplets are seen, at least two peaks are prominent in each cluster, three in some others. We have proposed that these FP peaks are more robust than those that would be obtained from standard Bragg mirrors in transmission for instance, because in a lossy mirror, transmission is generally mode degraded than reflection.

3. Nonlinear triple resonance

Ideally, in a structure equivalent to N FP in series, one could choose among any three peaks in a collection of 3N peaks to get as close as possible to equal spectral distances $|\omega_{\text{pump}} - \omega_{\text{idler}}|$ and $|\omega_{\text{pump}} - \omega_{\text{signal}}|$. For instance, a typical dispersion compensation would involve to choose peak1, peak1 and peak 2 or 3 respectively in each three-peak cluster of Fig.1(b), so as to restore the spectral distance diminished by material dispersion or flat waveguide dispersion. Another criterion is the overlap of the resonant fields. As each peak is a Bloch mode of the ensemble of N FP cavities, its repartition among the N resonators is specific in amplitude and phase. Thus, nonlinear effects may be coherently destroyed or reinforced, according to these amplitudes and phases, notably when one forms the field products $(E_{\text{pump}})E_{\text{signal}}$ for various cases and looks at their projection on $E_{\text{idler}}$ to see whether the nonlinear $\chi^{(3)}$ source term at idler frequency is on resonance or not. Our analysis based on known symmetries of Bloch modes has led us to discard single, double and triple FP and focus on $N=4$. We modeled the field in a four-FP structure thanks to a coupled mode model in the style of H. Haus [8], whereby each FP field evolution is resonant and fed by the adjacent cavities. For instance, a typical transmission spectrum is given in Fig.2(a). The Q factor of the system is around 5000, well in line with our experimental results. We also used the same approach to introduce scalar source terms acting on the whole field of each FP cavity, and we evaluated separately the “intra-cavity” overlap integral to check that the nonlinear source terms were well fed by the pump and signal fields. A typical result of such a modeling is the color map of Fig.2(b), which shows the strength of the nonlinear response as a function of the pump and signal frequency (causing the idler to be at $\omega_{\text{idler}}=2\omega_{\text{pump}} - \omega_{\text{signal}}$).

The enhancements are seen to be stronger with specific peaks. These are often the more resonant Bloch modes, i.e. the extreme ones of the four-peak clusters for one of the two frequencies, but not for both of them. The peak values occurring in this preliminary result, with a magnitude ~10-15, are not the absolute enhancements related to bulk propagation, prefactors ~ $Q^3$ have been omitted. More analysis is in progress, but the potential for highly enhanced triply resonant conversion is clearly identified.

In conclusion, we have evidenced the capability of broad waveguides to serve as resonators with a fundamentally simple structure. Such a structure is equivalent to multiple Fabry-Perot, although light never traverses mirrors but only uses reflection, a feature that we believe to be advantageous. Such system with its 4 peaks at each FSR can help compensate dispersion. A simplified coupled-mode model was used to analyze the condition of large $\chi^{(3)}$ enhancement for wavelength-converted signals. Here the magnitude of nonlinear third order response is found best on the extreme peaks.

References


Pulsed lasers have become new tools in the hands of conservators in several fields of cultural heritage preservation [1]. Mechanistic studies of the laser-induced detachment of microparticulates on polymeric bulk materials common in modern and contemporary art, such as, e.g., polyimide, polymethyl methacrylate, and foamed polyurethane, are still rare, and involve solely UV radiation. However, laser cleaning of biogenetic [1] and synthetic polymeric materials [2] can be successful with visible laser radiation [1,3].

In this study, visible 532 nm radiation was employed in order to guarantee minimum substrate interaction and maximum cleaning efficiency. Polymethyl methacrylate (PMMA), polycarbonate (PC), and polystyrene (PS) served as model substrates whereas graphite powder and PS beads as model contaminant dust. Evaluations were performed by electron microscopy, optical microscopic evaluations of modification areas, a light scattering technique, and laser-induced plasma breakdown spectroscopy.

References
PHOTON SYNTHESIS OF NANOMETRIC FILMS BASED ON TRANSITIONAL METAL OXIDES FOR MULTIPARAMETER SENSORS

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The reactive pulsed laser deposition (RPLD) based on a KrF laser was used for photon synthesis of nanometric iron and chromium oxides films. RPLD allows controlling the thickness and stoichiometry of deposits with definite band gap [1]. So RPLD was used for synthesizing nanometric iron oxides films for thermo-photo sensors [2]. We compared sensing properties of iron and chromium oxides nanometric films deposited on <100>Si substrate by RPLD. These iron and chromium oxides films have semiconductor properties with the band gaps less than 1.0 eV. Maximum value of thermo electromotive force (e.m.f.) coefficient of iron and chromium oxides films was about 1.65 mV/K and 3.5-4.5 mV/K, accordingly, in the temperature range 270 K to 290 K. The largest photosensitivity of iron and chromium oxides films was about 44 V/W and 2.5 V/W, accordingly, for white light at power density ~ 6x10^-3 W/cm². V_c is “chemical” photo e.m.f. Iron oxides films were tested as chemical sensors: the largest sensitivity of NO molecules was at the level of 7x10^12 cm³.

Our results showed that nanometric iron and chromium oxides films synthesized by UV photons can be used as up-to-date materials for multi-parameter sensors operating at moderate temperature.

References
APPLICATION OF LASER TEXTURING METHOD FOR MC-Si SOLAR CELLS FABRICATION

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The optimal regimes for uniform texturing of a multicrystalline silicon (mc-Si) surface by pulsed laser radiation have been determined. The results of laser texturing process application to mc-Si solar cells fabrication have been reported.

1. Introduction.
The main task of photovoltaics is to reduce the cost of electricity produced by solar panels. The most obvious trend in the manufacture of solar cells is to replace most expensive technologies with new ones. The investigations are currently being carried out to use the laser technologies in fabrication of contact structures (laser scribing for buried contacts, laser-fired contacts, depth-selective laser ablation, thin-film selective removal), in surface texturing to reduce reflection, in deposition of transparent conductive oxides, laser doping, etc. In the case of mc-Si solar cells the problem of reflective losses is very acute as the conventional methods of chemical surface texturing do not yield the desired result because of the randomized crystallographic orientation of multicrystalline silicon grains. So the development of the laser texturing method of mc-Si surface is very important task.

1.1 Experimental details.
Texturing was performed in the vacuum chamber by the beam of the second harmonic Q-switched Nd:YAG laser (532 nm). The 1 Ω·cm p-type mc-Si wafers were used. The Laminated Grid Cell (LGCell) solar cells [1] based on "black" mc-Si wafers have been fabricated and studied.

1.2 Results and discussions.
The uniformly texturized mc-Si samples with uniquely low total reflectance (less than 3%) in the wide spectral range of (0.3-1.1) µm have been produced. The influence of subsequent chemical treatment on the morphology and reflectivity of laser texturized samples have been analysed [2]. It is demonstrated that the application of the laser texturing method for the fabrication of the solar cells based on mc-Si has led to an increase in short circuit current density of ~5 mA/cm² and in external quantum efficiency (~18%) compared with the nontexturized reference cells. The efficiency of the laser texturized cells is higher than that of the nontexturized solar cells.
The results received demonstrate the potential of the laser texturing method for the mc-Si solar cells fabrication.

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References
Nano sized features on surfaces have a major influence on optical and mechanical surface properties. On glass and metal surfaces grating structure can serve as colorization and decoration. On reflective noble metals spike structure generate moth eye effects and therefore increase the absorptivity to up to 90% over a wide wavelength range[1]. For microfluidics the increased surface energy leads to hydrophobic exhibiting lotus effects[2]. These texturations are typically generated by applying femtosecond laser pulses with fluencies near the ablation threshold. Nearly all publications rely on a Ti:Sapphire laser for this type texturation. In contrast to this we demonstrate high repetition rate processing with YAG based femtosecond lasers. Examples of nanotexturation such as Figure 1 will be shown along with their application. As these nano features are known to be influenced by the polarization of the laser pulse [3] we engage radial and azimuthal polarization converters to manipulate the orientation of the periodic structures. The characterization of the surfaces is performed by means of SEM images, diffraction measurements and optical microscopy.

Figure 1: Hydrophobic metal surface due to femtosecond laser treatment

References
Femtosecond-scale polarization state shaping is experimentally found in optical response of a plasmonic nanograting by means of time-resolved Stokes polarimetry. Simultaneous measurements of the Stokes parameters as a function of time reveal a remarkable alteration of the polarization state inside a single fs-pulse reflected from a plasmonic crystal due to the excitation of time-delayed polarization-sensitive surface plasmons with a highly birefringent Fano-type spectral profile. Time-dependent depolarization, indicating the sub-130 fs polarization change inside the pulse, is experimentally found and described within an analytical model which predicts the fivefold enhancement of the polarization conversion effect with the use of a narrower time gate.

Introduction

Polarization is a fundamental property of an electromagnetic wave which describes the time-averaged trajectory of the electric field vector at a given point of space. The timescale over which the polarization is averaged is usually much greater than the period of a single electromagnetic field oscillation. However, various methods of femtosecond polarization shaping were proposed recently [1-6] which stimulated intense research in the field of quantum control [7, 8]. While many methods of femtosecond polarization shaping rely on conventional macro-scale optical devices, it is also possible to shape the polarization utilizing elementary excitations in submicron quantum-confined media [9, 10]. A convenient and easily tunable system for observing elementary excitations at room temperature is a spatially modulated surface of a noble metal film where surface plasmon polaritons (SPPs) are excited. Proved by numerous experiments involving femtosecond laser pulse sources [11-13], the mean lifetime of a resonantly excited SPP varies from tens to hundreds of femtoseconds in the visible and near IR spectral range peaking for dark modes, e.g., in SPP bandgap structures or plasmonic crystals [11, 12]. On the other hand, remarkable polarization-sensitive properties of plasmonic nanostructured media [14, 15] make it possible to use plasmonic nanostructures as polarizers [16] or waveplates [17, 18]. Despite high polarization performance and distinct temporal characteristics of anisotropic plasmonic materials, the ultrafast light polarization control with plasmonic media has not been observed yet.

In this work, we use time-delayed optical anisotropy of resonantly excited surface plasmon polaritons to realize an ultrafast control over the state of polarization (SoP) inside a single sub-picosecond telecom laser pulse reflected from a plasmonic crystal of subwavelength thickness. Time-dependent nonzero depolarization has been found which indicates the sub-130 fs polarization change inside the pulse.

1. Results and Discussion

The concept of the ultrafast polarization control with anisotropic plasmonic crystals, schematically depicted in Fig. 1, is based on the time-delayed nature of the SPP response. Incident pulse's SoP is split into two linear eigenmodes due to anisotropy of the sample and the p-polarized component is time-delayed via exciting SPPs. As a result, femtosecond polarization alteration is expected in the reflected pulse.

FIG. 1. Left: schematics of the ultrafast polarization conversion with plasmonic crystals. Sample dimensions are $D = 1.5 \, \mu m$, $d = 0.3 \, \mu m$ and $h = 50 \, nm$. Right: reflectance of the sample as a function of wavelength and angle of incidence (AoI) for p-polarized incident light. The dashed line denotes the AoI used for the ultrafast polarization conversion.

Observation of the ultrafast polarization shaping was performed on samples of plasmonic crystals fabricated by thermal sputtering of a gold film onto a polymer grating made by nanoinprint lithography. The following dimensions of the structure were chosen to match the SPP resonances spectral position to the central wavelength $\lambda=1.56 \, \mu m$ of the femtosecond laser source: the period is $D = 1.5 \, \mu m$, the duty cycle is $d/D=0.2$ and the film thickness is $h = 50 \, nm$. The
reflection spectra of the sample measured with p-polarized light with its E-vector perpendicular to the grating modulation are shown in Fig. 1. The minima associated with the band structure of SPPs coupled onto the surface of the film via the ±1st diffraction orders are revealed. The plasmonic bandgap is seen at the wavelength $\lambda = 1.52 \mu\text{m}$ with the width of $\Delta \lambda \approx 70 \text{nm}$, $\Delta \lambda / \lambda \approx 0.04$ which is comparable to the previous data on spectroscopy of plasmonic crystals [11, 12, 19].

Fig. 2 shows the intra-pulse SoP evolution for different values in terms of normalized Stokes parameters $s_i = S_i/ S_0$.

For $\psi = 0$ the SoP is a linearly Oy-polarized state for any time moment within the uncertainty of the method which is below 0.1 on the scale of Stokes parameter values. As $\psi$ is increased the modification of the SoP can be seen towards the end of the pulse. Various polarization transformations are observed at femtosecond timescale, e.g., switching between linearly polarized (aspect ratio 0.1) and right-hand circularly polarized (aspect ratio 0.8) is achieved in 100 fs at $\psi = 20$. Depolarization induced by the sample is seen in time dependences of the degree of polarization. The depolarization is a consequence of Stokes parameters averaging over the 130 fs-gate.

References
Laser-induced front and back side etching is a method for nanometer-precision etching of transparent materials using thin absorber layers. Within this study the etching of different amorphous and crystalline dielectrics (e.g., fused silica, boron crown glass (BK7), LiF, MgF₂, CaF₂, Si) with different metallic and organic materials (e.g., Cr, Al, Mo, toluene) is presented using short and ultrashort laser pulses with wavelengths from ultraviolet to infrared. As laser sources, an excimer laser with a wavelength of 248 nm as well as 351 nm and with a pulse duration of 25 ns, a Nd:YAG laser with 355 nm, 532 nm as well as 1064 nm and 10 ps, and a Ti:sapphire laser with 780 nm and 150 fs were used, respectively. The influence of the substrate and absorber properties as well as of the laser parameter on the back and front side etching process was analysed. The etched surfaces were analysed with microscopic (white light interferometry, scanning electron microscopy (SEM)) and spectroscopic methods (X-ray photoelectron spectroscopy (XPS), energy dispersive X-ray spectroscopy (EDX), Rutherford backscattering spectrometry (RBS)). The results show: at moderate laser fluences, the etching depth increases linearly with the laser fluence and rises exponentially with the adsorber layer thickness. Furthermore, the etching depth increased with decreasing wavelength and increasing pulse duration.

1. Introduction
The structuring of dielectrics with lasers allows a high flexibility and an efficient production of complex structures. However, the precise machining of transparent materials with well-defined etching depth and a low surface roughness, e.g., for micro-optical applications, is a challenge for laser processing. The direct ablation using VUV, ps, and fs lasers [1, 2] and excimer laser radiation at high laser fluences [3, 4] afford the structuring of dielectrics. However, the direct ablation method can tend to an increased surface roughness. A better alternative for structuring is the usage of thin adsorbing layers to absorb the laser radiation. Based on this concept, different methods were developed, e.g., laser etching using a surface-adsorbed layer (LESAL), laser-induced back side dry etching (LIBDE), laser-induced back side wet etching (LIBWE) [5–7], and laser-induced front side etching (LIFE) as well as laser-induced front side etching using a self-regenerating adsorber layer (SAL-LIFE). These methods allow the fabrication of nm-precision high-quality etching trenches with a low surface roughness.

2. Experimental set-ups
In the following study different back and front side etching methods were used for structuring different dielectrics. As absorber layer different metal layers (LIBDE and LIFE) and toluene (LESAL and SAL-LIFE) were used. For the metal layer, the polished surface of the samples was coated by magnetron-sputtering with metal layers of different thickness. The toluene surface modification was achieved by a pressure-controlled toluene gas phase in a vacuum chamber. The covered surfaces were irradiated with different lasers having wavelengths from ultraviolet to infrared and pulse widths ranging from nanoseconds to femtoseconds. In particular, an excimer laser with a wavelength of 248 nm as well as 351 nm and a pulse duration of 25 ns, a Nd:YAG laser with 355 nm, 532 nm as well as 1064 nm and 10 ps, and a Ti:sapphire laser with 780 nm and 150 fs were used, respectively. The excimer laser radiation exhibits a top hat profile and the Nd:YAG as well as the Ti:sapphire radiation has a nearly Gaussian beam and higher harmonic profiles, respectively. The top hat profile was formed by a beam shaping and homogenizing optics with an intensity deviation in the mask plane of below 5% rms. The laser fluences, the repetition rates as well as the pulse numbers per area were varied. The etching depth as well as the surface roughness was measured by white light interferometry (WLI). Furthermore, the surface was imaged by scanning electron microscopy (SEM) and the samples was analysed by Rutherford backscattering spectrometry (RBS), X-ray photoelectron spectroscopy (XPS) as well as energy dispersive X-ray spectroscopy (EDX).

3. Results and discussion
The etching depth induced by different laser radiation was measured for the different absorber layer – substrate combinations by WLI. Selected examples are shown in figure 1. In figure 1 (left), the etching depth in fused silica (for a chromium – fused silica system) is presented for a ns laser radiation with a wavelength of 248 nm and 351 nm and front and back side etching geometry. In conclusion, the etching depth can be analytically described by Eq. 1 [8]:

\[ d(\Phi, \Delta z) = \delta_1 \cdot \left( \Phi - \Phi_{th} \right) \cdot \left( 1 - \exp(-\sigma_\delta \cdot \Delta z) \right) \cdot \left( 1 - R(\Delta z) \right) \]  

(1)
Figure 1: (left) Dependency of the etching depth of fused silica on the laser fluence (left) for a chromium layer thickness of 5 nm and 10 pulses (For a 5 nm thick metal layer no pulse dependency occurs, \( d(1 \text{ pulse}) \approx d(N \text{ pulses}), N = 2-10 \)) and the dependency of the etching depth on the layer thickness (right) for a constant laser fluence of 9.3 J/cm\(^2\) and 2.9 J/cm\(^2\), respectively with 10 pulses per area for laser-induced front side etching (LIFE) and back side etching (LIBDE) at XeF (\( \lambda = 351 \text{ nm} \)) and KrF (\( \lambda = 248 \text{ nm} \)) laser radiation, (points: measured etching depth, curves: adaptation of Eq. 1). (right) Surface morphology of the irradiated fused silica (with chromium layer) for back and front side etching geometry (2.6 J/cm\(^2\), XeF laser radiation) measured at white light geometry.

with \( d \): etching depth, \( \Phi \): laser fluence, \( \Delta \): layer thickness of absorber layer, \( \delta \): slope coefficient, \( \Phi_{\text{th}} \): ablation threshold, \( \alpha \): virtual absorption coefficient, \( R \): reflectivity. The found analytical equation also describes the etching depth behaviour for fs and ps laser radiation with wavelengths from infrared to ultraviolet.

Furthermore, the irradiation allows the well-defined and smooth removal (roughness \( \leq 10 \text{ nm rms} \)) of the fused silica; the surface morphology is presented in figure 1 (right). Further information can be found in [8-11].

4. Conclusion
The possibility of the production of nm-precision and smooth surface structures by laser-induced front and back side etching processes was studied for different wavelengths from 248 nm to 1064 nm and pulse durations from 150 fs to 25 ns. For all lasers used a similar behaviour was found. The direct comparison of the different pulse durations is difficult due to the different wavelengths, and the ns and ps laser radiation interactions present a distinct wavelength dependency. However, taking into account the maximum achievable etching depth within each of the laser etching process windows a trend is visible. The etching depth decreases for longer wavelengths and increases with longer puls durations. Furthermore, the etching depth achieved for the laser-induced back side etching process is higher than that for the laser-induced front side etching.

References
INVESTIGATIONS OF THE SINTERING OF THE OVERHANG LAYERS

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Abstract: Investigation of the sintering of overhang layers has been conducted under full temperature control and Rayleigh - Taylor instability of the contact surface between melt and powder in a gravity field was found. The optical monitoring system provide the possibility to measure spatial distribution of brightness temperature at two wavelengths and selected temperature profiles, calculation of colour temperature and maximum temperature in focal spot. RT instability progress under laser radiation action causes the complete loss of stability of the molten layer with a dip to the loose powder bed.

1. Introduction

SLM technology has difficulties in building an overhang plane due to the process definition of layered wise production in a powder bed. Routinely this problem can be solved using support structure which afterwards have to be removed by post processing. Another way consists in investigation of the this phenomena and control of the melting process. The system was developed [1] for monitoring of temperature distribution in laser irradiation zone based on registration using a high speed digital CCD – camera and maximum temperature measurements in laser spot by pyrometer. Using a calibrated pyrometer and camera allows to fully control the process of sintering/ melting [2]. The developed optical monitoring system has been used in studies of sintering of the overhang layers and the results of studies are presented in this paper.

2. Experimental

In this study the PM 100 machine of Phenix Systems with the typical for this kind of equipment design was used. The source of radiation is a YLR-200 cw fiber laser with a maximum power P = 200 W, the wavelength \( \lambda = 1075 \text{ nm} \) and the laser spot size \( d = 75 \mu m \). In these experiments, a some layer of Cu (-63 + 20 \( \mu \)m), CoCr and W powder 25 \( \mu m \) in diameter was deposited using a usual powder feeding system (a scrape blade). In some experiments oxide copper powder was used for greater laser radiation absorption. The thickness of loose powder bed was 3 -6 mm. Overhang layers were scanned with scan shift (hatch distance) 30 \( \mu m \) under temperature control. The small hatch distance was selected for a smooth surface production. Only one cross-section 100 x 100 mm\(^2\) was scanned with the scan speed 100 mm/s. Experiments was conducted in \( \text{N}_2 \) and \( \text{Ar} \) atmosphere. The brightness temperatures resulting from experiments have been transformed to thermodynamic temperatures using emissivity data: for Cu - \( \varepsilon = 0.1 \); W - \( \varepsilon = 0.3 \); CoCr - \( \varepsilon = 0.35 \) [4,5].

3. Results and discussion

The small loose powder bed thermal conductivity results in too large heat input during scanning of an overhang layer, thick melt pool formation, which sink in the powder bed. Mechanism of the melt penetration into loose powder bed has not been investigated and threshold conditions have not been determined. Accumulation of heat in the layer affects the flow of the melting process, encouraging the development of the instability of the contact surface between the melt and powder in a gravity field. Observed structures on the contact surface between melt and powder (fig.1) are typical of the Rayleigh - Taylor (RT) instability [6]. When the layer of melt is located on a layer of powder with a density of \( \sim 0.5 \) of the melt most intensively will rise perturbations with a wavelength \( \lambda_m = 4\pi (\alpha \nu^2 / g)^{1/3} \) equal cm. Linear increment \( \tau = (g \cdot 2\pi / \lambda)^{1/2} \) of perturbations growth is \( 3 \cdot 10^2 \) 1 / s.). Small thickness of the melt leads to the formation of hollow conical spikes and pores on the surface (Fig.1 a,b). The maximum surface temperature during melting of Cu layer reached 2000 K - 2300 K. In such conditions the melt boiling is absent and recoil pressure can not cause melt pool sink into the powder bed.

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Figure 1: Structure of overhang layer. (a) – bottom view, (b) – end view, (c)– brightness temperatures in melted area, (d) - frame recording, exposure time - 0.05 s. Powder – Cu, - 60 +20 \( \mu \)m, P = 80 W.
The measurements of the maximum melt temperature in area 130 µm in diameter by pyrometer in combination with the measurements of the temperature distribution by CCD-camera in synchronism with frame recording were conducted.

It has been found that at the start of scanning laser radiation acts on the individual particles through low thermal conductivity of the powder bed and causes their overheating (fig.1). Calculation of the heating of a single Cu particle under action of the laser power of 80 W has been conducted. The temperature of copper particle reaches $2 \times 10^3$ K, which is consistent with the value measured in the experiment. Temperature fluctuations are observed during 3s (fig.1c). They are associated with the interaction of the laser radiation with structures originated on the melt surface (fig.1d). The time taken to their growth is estimated at 0.1s.

When scanning the layer of powder with high thermal conductivity of the particles material the front of melting moves directly ahead of the laser track. Melt layer is subject to instability and the surface structure is formed with a grooves considerable depth. These surface structure has high absorptivity. The result is the rise of surface temperature in these areas, increase the recesses during scanning of these structures.

Also the increase in the melt spot and the manifestation of several spots has been observed due to multiple reflections of the laser radiation in the pits. The second mechanism of super-deep penetration of the laser radiation in a powder bed is associated with balling effect. Large drops of melt draw nearby powder with resulting laser radiation penetration at a depth up to 2 mm.

When scanning a loose powder bed from powders of CoCr, steel 316 with low thermal conductivity and higher absorptivity the melt front did not overtake the scan track. At the start of the scanning the particles overheating also takes place. Some melt regions are formed then merged into continuous melt layer. Instabilities which sink to powder bed also are seen but in most cases at the border of the scan area where scan spot is stopped and overheating takes place.

**Conclusion**

Investigation of the melting of the overhang layers has been conducted under full temperature monitoring. The mechanisms of the melt penetration into loose powder bed have been determined:

1. Accumulation of heat in the molten overhang layer results in the development of the instability of the contact surface between the melt and loose powder in a gravity field - Rayleigh - Taylor (RT) instability. RT instability progress under laser radiation action causes the complete loss of stability of the molten layer with a dip to the loose powder bed.
2. The second mechanism of super-deep penetration of laser radiation in a powder bed has associated with balling effect. Large drops of melt draw nearby powder with resulting laser radiation penetration to a depth up to 2-3 mm. In either case the destruction of layer is associated with a overheating and after a lapse of time (3 s) the process passes to steady state with surface temperature 1500 K for Cu powder because the previously melted material act as a heat sink.

**References**


LASER INDUCED HYDRODYNAMICS FOR BIOTISSUE REGENERATION

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Hydrodynamic effects induced in water by medium power (1–5 W) CW laser radiation delivered via an optical fiber are reported. The effective hydrodynamic processes in water are related to the explosive boiling in the vicinity of the heated end surface of the fiber. The resulting bubbles with sizes ranging from several to several tens of microns have velocities of up to 100 mm/s in the vicinity of the end surface. The generation of bubbles in a capillary gives rise to the stable circulation of liquid with the period ranging from 0.2 to 1 s. These hydrodynamic effects can be employed effectively for surgical and regenerative procedures.

Modern laser medical technologies widely employ delivery of laser light to irradiated tissues via optical fibers. Optical fiber easily penetrates through needle and endoscopic channels, and laser light can be delivered through a fiber for puncture and endoscopic operations. Several laser medical technologies (puncture multichannel laser decompression of disc, laser intervention upon osteochondrosis, surgical treatment of chronic osteomyelitis, endovenous laser ablation, etc.) are based on effective hydrodynamic processes in water-saturated biotissues. Laser irradiation of water and water-saturated biotissues causes formation of micro-bubbles and their streams, circulated flows of liquid and even filaments [1-3]. These hydrodynamic processes trigger cellular response and regenerative effects through the specific mechanisms of mechano-biology [4]. They can stimulate sanitization of degenerated tissue cavities and proliferation of cells [5]. We consider here different kinds of effects stimulated by a medium power laser-induced hydrodynamics in the vicinity of a fiber tip surface, in particular, generation of vapor-gas bubbles, fiber tip degradation, and generation of intense acoustic waves.

We have performed the measurements in bulk liquid and in the glass capillary that simulates the laser channel. A developed threshold character of the dynamics of liquid is demonstrated. At a relatively low laser power (about 1 W), we observe the slow formation of air–vapor bubbles with sizes of hundreds of microns on the end surface of the optical fiber. The bubbles can be attached to the end surface during the irradiation session. When the laser power increases, we observe the hydrodynamic processes related to the explosive boiling in the vicinity of the hot end surface (Fig.1).

The resulting bubbles with sizes ranging from a few microns to several tens of microns provide motion of liquid. The estimations give a velocity of up to 100 mm/s for the bubbles in the vicinity of the end surface. The generation of bubbles in the capillary leads to the circulating liquid flows with periods ranging from 0.2 to 1 s. Note that the circulation intensity increases with the laser power. For the laser radiation with a wavelength of 0.97 µm, we observe such effects only for the blackened end surface of the silica fiber, which serves as a point heat source. At a laser power of less than 3 W, stable bubble microjets, which consist of the bubbles whose sizes range from several to ten microns, can be generated in the vicinity of the blackened end surface.

Figure 1. The generation of microbubbles in the vicinity of the blackened end surface of the optical fiber in water for the laser radiation with a wavelength of 970 nm and a power of (a) 1 and (b) 5 W.

The arrows show the points where the jets loose stability.

Figure 2. Bubble microjets in the vicinity of the schematically shown end surface of the optical fiber.
Hydrodynamics caused by laser heating in the free liquid volume can lead to the degradation of the fiber end surface over several minutes even at relatively low laser intensities ($10^3$–$10^4$ W/cm$^2$). The hydrodynamic processes in the regime of the channel formation result in more significant modifications over shorter times. In this regime, a channel is burnt by the laser-heated fiber end surface in the presence of water in a wooden bar that mimics the biotissue. Holes and cracks appear on the fused working surface, and the structure of the silica fiber in the vicinity of the end surface appears damaged. Even at moderate laser powers and intensities of about $10^4$ W/cm$^2$, the temperature in the vicinity of the end surface of delivery fiber can reach several thousand degrees. High temperatures and pressures resulting from the collapse of the cavitation microbubbles allow growing of a new phase (nanosized diamonds) and the formation of the supercritical water, which also facilitates the degradation of fiber [3]. The observed significant degradation of the delivery fiber due to multiple irregularities of different scales, causes substantial modification of the irradiation of biotissues.

Laser-induced hydrodynamic effects are accompanied by high-intensity acoustic signals in a wide frequency range (up to 10 MHz and even greater) (Fig. 4).

Laser induced hydrodynamics allows:
- Triggering biotissue regeneration;
- Sanitization of biotissue cavities;
- Bloodless and precise cutting of biotissue;
- Stimulate cell membranes permeability and drug delivery.

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References
LASER TISSUE SOLDERING USING NANOPARTICLE-DOPED ELECTROSPUN POLYCAPROLACTONE SCAFFOLDS

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The use of a poly-caprolactone (PCL) scaffold doped with dye packed nanoshells and bovine serum albumin (BSA) has been shown to improve tissue fusion in laser tissue soldering (LTS). However, the flow-off causing dilution of the solder and thus the reproducibility remain challenges. This study investigates the possibility of using an electrospun PCL-scaffold doped with dye containing nanoparticles for anastomosis. In addition, we designed a plug-shaped solder carrier for Natural Orifice Transluminal Endoscopic Surgery (NOTES). This plug has been successfully used to close gastric incisions in an in-vivo study.

1. Introduction

Laser tissue soldering is a powerful technique for sutureless fusion of tissue or closure of blood vessels. Previously, a method was developed that applies a solder doped PCL scaffold for LTS [1-3]. Briefly, in LTS, a chromophore (indocyanine green, ICG) enhanced protein solution (bovine serum albumin, BSA) is added to the tissue fusion side and laser energy is deposited in the solder leading to denaturation and finally to the fusion of the fission [4]. The main problem still to be solved is stabilizing the ICG in the scaffold. This project is aiming at optimizing this scaffold.

One objective of this study was the development of a particular nanoparticle (NP) system in order to stabilize ICG fluorescent dye in aqueous media for LTS. In our previous study, ICG encapsulated nanoshells were already developed, but the ICG concentration and their photo-stability was low. Therefore we developed a 2nd generation of NP’s based on a solid silica sphere covered with ICG doped polycaprolactone and an additional layer of poly (L-lactide) for stabilization. These NPs can be produced with a high ICG concentration and they show a very good photo-stability.

The second objective is the incorporation of the nanoparticles and BSA into a PCL scaffold by electrospinning [5]. This method enables quantitative binding of ICG and BSA. Electrospinning parameters, including electric voltage, gap distance, feed rate and solution parameters, were investigated and the fibre morphology was observed using scanning electron microscopy.

Furthermore, a solder doped scaffold based on the same processing method can be used for gastric closures. Previously, we designed a plug-shaped, PCL-based solder carrier that can be soldered into the gastric incision and onto the mucosa. The next step will be to realize form electro-spinning to directly produce the plug.

Finally, in vitro LTS is performed on rabbit aortas using a continuous wave diode laser at 808nm. Scaffold surface temperatures were analyzed with an infrared camera and the tensile strength of the tissue was measured. Gastric closure was performed in vitro using porcine stomach. The healing of the injury site and the internal leak pressure was determined.

2. Materials and Methods

2.1 Preparation of ICG doped nanoparticles

A core shell nanoparticle system was developed consisting of a silica core with a target diameter of about 80 nm and a hydrophobic polymer shell acting as a carrier system for the ICG. In the next step, the particles were coated with L-Lactide leading to a hydrophilic outer shell. The ICG loaded NP’s were characterised by scanning electron microscopy (SEM) and analyzed by Infrared Spectroscopy (IR).

2.2 Electrospinning

For electrospinning a solution of 9% wt. PCL in chloroform/methanol (75/25 v/v) mixture was pumped into a syringe needle of 21 G. The grounded electrode was located 15 cm from the needle tip. The applied voltage was set to 15 kV. The feed rate of the solution was 30 µL/min to maintain a constant supply of polymer.

2.3 Model for soldering procedure

The feasibility of this soldering technique was studied by assessing the local heating of the area and tensile strength of the resulting fused tissue. Therefore, rabbit aortic arteries were soldered using a “sandwich technique” that kept the two vessels in close contact during the laser soldering. As laser source a GaAlAs diode laser system emitting continuous wave radiation at 808nm was applied. During soldering an infrared camera was used for temperature recording. A test stand with a fixed force gauge was used to measure the tensile strength.
2.4 In vitro gastrotomy closure
The cylinder of the plug was manually inserted into the gastrotomy before soldering the disk to the gastric mucosa. A lens-shaped multimode quartz fibre was used to irradiate the plug with light from a diode laser with a power of 2.9 W.

3. Results
Silica core nanoparticles with ICG embedded into a hydrophobic polymer matrix were developed (Fig. 1). Using this approach, the dye was stable in the scaffold even in aqueous media, which guarantees that no dye can leach out of the scaffold during handling and soldering.

Electrospinning produces a matrix that is mechanically strong and elastic to be easily applied during anastomosis (Fig. 2). The ICG-nanoparticles are entrapped into the matrix during the process without further modification. The next step is to spin BSA directly with the PCL solution, instead of soaking.

The in vitro and preliminary in vivo experiments showed that an endoscopically placed secure closure of a gastrotomy is feasible with LTS plugs. Leak pressure is high and technical handling seems to be easy. Our data suggest that this method may have advantages compared to other closure techniques.

4. Acknowledgement
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References
In this paper the influence of spatial and energy characteristics of Er-lasers radiation on some optical and mechanical properties of human hard tooth tissues were studied. Thresholds of effects to the enamel and dentin which are initiated by action of laser radiation with an energy density below the ablation threshold of tissue were examined. It was found that the multi-pulse impact of Er-lasers radiation with pulse energy below the ablation threshold promotes changes in the reflective index of enamel and the microhardness of enamel and dentine.

1. Introduction
Today Er–lasers with wavelengths near 3 microns are widely applied to ablation of hard tooth tissue [1]. The wavelengths are close to peaks of enamel and dentine absorption. The effects which are initiated in hard tooth tissues by action of Er-laser radiation with an energy density below the ablation threshold are of significant interest. This paper is devoted to the influence of spatial and energy parameters of erbium lasers radiation on the optical properties of tissue: the reflective index, and mechanical properties of tissues: enamel and dentine microhardness. Such research can open new perspectives in esthetic and preventive dentistry. In the work we use lamp pumped YAG: Er laser ($\lambda=2.94$ µm) and new diode pumped YLF: Er microlaser which irradiates in wavelengths range of 2.6–2.9 µm. Advantages of diode pumping of YLF: Er laser are: possibility of more effectively conversion of pumping energy to generation energy; simple change of wavelength, pulse duration, pulse repetition rate and spatial distribution.

2. Effects in hard tooth tissues
In this work enamel and dentine treatment was carried out by YLF: Er laser radiation with wavelength of 2.84 µm, at single–pulse impact. Pulse energy reached 2 mJ in treated area at pulse duration of 150–300 µs, 3.5 mJ at pulse duration of 300–700 µs, and 4.5 mJ at pulse duration of 700–1000 µs. We observed some effects as a result of laser radiation impact: modification (whitening), destruction (crater formation) and carbonization. Modification (whitening) of enamel was observed at pulse energy of 0.5–1.4 mJ and pulse duration of 270–955 µs. This effect was observed for dentine at 0.4–0.7 mJ and 270–930 µs. Enamel destruction occurred at pulse energy of 1.1–2.2 mJ and pulse duration of 285–980 µs. This effect was observed for dentine at 0.8–1 mJ and 280–940 µs. Enamel carbonization was not observed at impact of YLF: Er laser radiation. Dentine carbonization was observed at pulse energy of 1.6–2.2 mJ and pulse duration of 300–980 µs.

3. Optical properties
It was shown that the reflective index of tooth enamel can be changed by the impact of erbium laser with subthreshold energy densities. The value of laser induced changes in reflectance depends on the laser energy density and number of laser pulses delivered to a single point on the sample surface. For YAG: Er laser radiation, the enamel reflection can be increased by 20% or decreased by 10% compared with the intact tissue reflection, as a result of changes in energy density and the number of laser pulses.

4. Mechanical properties
In [2] it was shown that the use of laser radiation both independently and in combination with the use of fluoride reduces enamel solubility in acid and increases its microhardness. It is also noted that dentin structures become denser under the action of laser radiation with subthreshold energy densities [3]. According to modern concepts, such effects in tissues appear due to local heating (from 100 to 1100ºC) which leads to the structural, chemical and crystalline changes in tissues [4–6]. It has been previously investigated the influence of carbon dioxide, erbium, holmium, excimer, and argon lasers radiation on the permeability of the solubility in acid and microhardness of tooth hard tissues [2, 4, 6–9]. In this paper investigation of the new diode pumped YLF: Er microlaser ($\lambda=2.84$ µm) radiation influence on the microhardness of enamel and dentine was carried out for the first time.

We used laser energy below the threshold of whitening effect. As a result of our experiments it was found that dentine microhardness is increased by 35% compared with intact dentine after laser radiation impact with the laser pulse energy – 0.25±0.03 mJ, laser pulse duration of 290±15 µs, pulse repetition rate of 250 Hz, number of laser pulses of 55, the tissue treatment with step near 80 microns. Enamel microhardness is increased by 25% compared with intact enamel...
after laser radiation impact with the laser pulse energy of 0.90±0.09 mJ, laser pulse duration of 285±15 µs, pulse repetition rate of 3 Hz, number of laser pulses of 100.

References
ENGINEERING THE CELLULAR NICHE USING BIOPOLYMER PATTERNS ON DIFFERENTIALLY ADHERENT SUBSTRATES

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Idealized cellular niches fabricated from different cells and biomaterials would be excellent platforms to study the cellular interactions found in natural microenvironments. We report on the fabrication of idealized cellular niches by applying the laser-based cell printing technique to reproducibly and rapidly deposit mouse embryonic stem cells at the cell-by-cell level and in a CAD/CAM fashion, onto receiving substrates that have novel patterns of fibronectin extracellular matrix biopolymer deposited by laser deposition. All MAPLE-deposited fibronectin patterns have been obtained through shadow masks by varying geometry and thickness. The biopolymer coatings served as biocompatible coating for the temporary immobilization of the stem cells, laser absorbing material for cell transfer, cushion for cell deposition on the receiving substrate, and medium for subsequent cell growth and organization. Immediately after transfer, the myoblasts spatially recognized their local two-dimensional environments and spatially manipulated their adherence and growth to form organized tissue. While cells in a culture flask grow in random directions, the laser-transferred cells deposited near one another immediately begin to organize. This behavior has showed that the immediate spatial organization of mammalian cells has played a dominant role in the subsequent tissue formation, and this organization has been extended to macroscopic dimensions.
USING FS-LASER PULSES TO SELECTIVELY KILL SPECIFIC
CELLS INSIDE TOMATO MERISTEMS — INVESTIGATION OF LEAF
PATTERNING

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The mechanisms responsible for phyllotactic patterns in plants are not yet fully understood. Auxin, together with
the transport protein PIN1, is commonly held responsible for phyllotaxis. In this study, we use an amplified
femtosecond laser source to ablate specific regions inside the primordium in PIN1:GFP tomatoes without
affecting the viability of cells adjacent to the ablated region. Targeted ablation of PIN1:GFP expressing
provascular cells can thus be effectively achieved. This allows the investigation of the role of the PIN1 protein
and of the different cell types and cell layers in plant organ formation.

1. Introduction

New leaves and flowers originate from the shoot apical meristem in the plant. The regular arrangement of these organs
around the stem in a plant is known as phyllotaxis, defined by the divergence angle between two successive leaves. The
meristem is made of a group of undifferentiated cells arranged in three layers, with the outermost layer denoted as L1,
followed by the subepidermal L2 layer. L3 is the internal mass of cells and divides in a much more random fashion. L1
and L2 are maintained by stereotyped cell division patterns, leading to separated cell lineages.1 The L2 and L3 layer
together form the ground tissue. It is assumed that for organ formation some sort of communication between the
different cell layers have to occur.2 Different mechanisms have been proposed, such as biophysical forces or directed
signaling molecule transport. Nowadays, it is commonly assumed that leaf initiation, separation and spacing are dictated
by auxin dynamics. Polar auxin transport by the auxin efflux carrier PIN13 yields the formation of auxin maxima
(convergence points) within the meristem, thereby deciding the position of the future primordium. Steeves et al.4
hypothesized that auxin dynamics in the meristem are sufficient to generate phyllotactic patterns and initiate
vasculature. Current phyllotactic models are also based on the L1 auxin fluxes driven by PIN1 expression.3,5,6,7
However, recent work has demonstrated that PIN1 is extensively expressed in the ground tissue.8 It is likely that the
vasculature within the ground tissue also influences the plant patterning in the shoot apical meristem.9,10,11

Tomato plants show spiral phyllotaxis with a divergence angle of 137.5°. The primordia, the leaves in their youngest
form emerging from the shoot apical meristem, show an up regulation of PIN1:GFP around the cells that will form the
future midvein. We ablated the PIN1:GFP expressing provascular cells in the youngest primordium (P1) of tomato
meristems without affecting adjacent regions, and we can therefore test for the influence of this site on the leaf
patterning.

2. Materials and Methods

13 day old PIN1:GFP tomato saplings, grown on tomato meristem culture, were dissected up to P2. The primordia are
named P₀, P₁, P₂ … Pₙ in the ascending order of their age. On the other hand, the oldest incipient primordium is called I₁
followed by I₂ and so on. The apices were stained with propidium iodide (4 mg/l) for 5 minutes prior to the ablation
experiments to gauge for cell damage.

A Nikon A1R MP confocal laser-scanning microscope (Nikon Instruments Europe B.V., Amstelveen, The Netherlands)
was used for confocal microscopy to image the meristems. For cell ablation, an amplified femtosecond laser (Coherent
RegA 9050, seeded by a Coherent Mantis, single shot, pulse duration 80 fs; Coherent Inc., Santa Clara, California) was
used at 800 nm. Both for viewing and ablation we used a 60x 1.27 NA water dipping objective, providing a lateral
resolution of about 250 nm.

To kill a specific region around the midvein of P₁, one or multiple stimulation points were set in one scan plane. These points were treated using a double shot from the RegA laser at a wavelength of 800 nm, a shot to shot time of 4 µs and an irradiance of about 1 PW/cm². The whole meristem
was then scanned again in 3D by confocal microscopy to gauge for the extent of damage delivered.

The meristems were then followed over three days by rescanning them using confocal microscopy every day. Afterwards, the growth of the samples was monitored for 10 days using a VHX-600 light microscope (Keyence NV/SA,
Mechelen, Belgium), changing the media every day.

Control samples were imaged using the same protocol, but no cell killing was done.
3. Results

Figure 1 shows a two photon scan before (left) and after double shot femtosecond ablation (right) of the same plane in the meristem; the PIN1:GFP is shown in green, while the dead cells that have internalised propidium iodide are shown in red. It can be seen that a confined region (two cells) inside the meristem in L3 was efficiently killed. Using this method, one or multiple ablation sites can be targeted and the affected cells can therefore be tested for their function inside the meristem.

Depending on the laser parameters used and the ablation sites chosen, different outcomes were observed. When the forming midvein of P1 is targeted and two to three cells are killed, the midvein path is reformed around the affected site and the primordium grows normally. Ablation of ground tissue of more than three cells usually results in a terminal differentiation of the meristem, but the primordia already present grow normally, and sometimes an auxiliary meristem takes over, continuing the growth of the plant. The ablation of L1 cells in several places on the other hand doesn’t seem to influence the meristem; it keeps growing normally.

![Figure 1: Before (left) and after (right) femtosecond shot confocal image of a tomato meristem. The slice is perpendicular to the growth axis of the plant. The green channel shows the PIN1:GFP, the red channel the internalization of propidium iodide due to cell death. The femtosecond laser has been targeted to cells in L3.](image)

The control samples all grew normally, showing that the observations can be attributed to the femtosecond laser treatment.

These initial results indicate that the femtosecond laser aided cell ablation can be used to determine the signaling pathways involved in phyllotaxis and will help us to shed light on the still unknown mechanisms.

References

COLOUR SENSOR WHITE BALANCE INFLUENCE ON WHITE-LIGHT INTERFEROMETER RESOLUTION

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Impact of a sensor color balance on white-light full-field optical coherence tomography (FF-OCT) resolution is investigated in the paper. Full width at half magnitude (FWHM) of a coherence pulse was calculated for various white balance (WB) settings. The dependence of FWHM on WB of a sensor in halogen lamp and white LED cases is shown in the paper. The minimum interference pulse width can be achieved by the proper color balance coefficients choice. And in this case the pulse is narrower than either one registered by colour image sensor with WB based on light source emission spectrum or by monochrome image sensor.

1. Introduction

White-light full-field optical coherence tomography (FF-OCT) is a well-known technique for cell level tissue inner structure investigation [1-3]. The main advantage of the technique is a high spatial resolution in transverse and longitudinal directions. The latter is due to wide effective spectrum of a probing light [4, 5]. It is shown in [6] that the width of the effective spectrum is determined by impact of all components of the interferometer on a light source emission spectrum. Assuming optical elements such as mirrors, beamsplitter and microobjectives are perfect, one may consider a spectral response of a detector has a determinative influence on the effective spectrum [7].

In the work we demonstrate a possibility of summarized effective spectrum shaping by changing colour image sensor spectral response using white balance (WB) correction. A dependence of interference pulse width and white-light interferometer resolution on WB coefficients is shown. Also a possible increase of interferometric system resolution compared with one may achieved using general color correction based on the type of the source is noted.

2. Interference signal acquisition with colour sensor

The effective spectrum of light $S'_D (\lambda)$ is described by an expression [6]:

$$ S'_D (\lambda) = S_D (\lambda) - S_S (\lambda), $$

where $S_D (\lambda)$ is the spectral sensitivity of the detector and $S_S (\lambda)$ is a light source emission spectrum. When the spectral response of each colour channel $S_R (\lambda)$, $S_G (\lambda)$ and $S_B (\lambda)$ is given, the summarized effective spectrum could be written as:

$$ S'_{RGB} (\lambda) = S'_{RGB} (\lambda) - S'_{S} (\lambda) = S'_R (\lambda) + S'_G (\lambda) + S'_B (\lambda), $$

where $S'_R (\lambda)$, $S'_G (\lambda)$ and $S'_B (\lambda)$ are the effective spectrums of those portions of light which generate an interference patterns in the corresponding colour channel and $S'_{RGB} (\lambda)$ is the summarized sensitivity spectrum of colour detector.

According to the Wiener-Khintchine theorem [4] coherence function of light with the summarized effective spectrum is equal to weighted sum of the partial coherence functions:

$$ \tilde{A}_{RGB} (\Delta) = \sum_{c=R,G,B} k_c \tilde{A}_c (\Delta) = \sum_{c=R,G,B} k_c \int_0^\lambda \frac{1}{\lambda^2} S'_c (\lambda) e^{i{2\pi \lambda \Delta / \lambda}} d\lambda = \int_0^\lambda \frac{1}{\lambda^2} S'_{RGB} (\lambda) e^{i{2\pi \lambda \Delta / \lambda}} d\lambda , $$

where $\Delta$ is the optical path difference, and $\lambda$ is the wavelength of light, $k_c$ is the white balance coefficient corresponding to the colour channel $c$, $S'_c (\lambda)$ is the spectral response of colour channel $c$, $S'_{RGB} (\lambda)$ is the summarized effective spectrum and $\tilde{A}_{RGB} (\lambda)$ is the summarized coherence function. White balance coefficients are taking into account in both $S'_{RGB} (\lambda)$ and $\tilde{A}_{RGB} (\lambda)$.

3. An impact of various white balance correction on interference signal

In the paper we analyze the full width at half magnitude (FWHM) of the coherence function to estimate the impact of the white balance correction. As follows from (3) only the color balance coefficients determine a shape of the summarized coherence function for the given image sensor and light source. Therefore the coherence function width $l_{source}^{RGB}$ is a function of three variables $l_{source}^{RGB} (k_R, k_G, k_B)$. For convenience we can fix one of coefficients ($k_G = 1$) and change the others. Therefore the interference signal width can be represented as a two variable function $l_{source}^{RGB} (k_R, k_B = 1, k_B)$.
Dependence of the coherence function width \( I_{3200} \) on the white balance coefficients is shown on Fig. 1a. The data is valid for halogen lamp operating at 3200°K temperature. The triangle-marked curve indicates a set of vectors \( \mathbf{k} = (k_R, k_G, k_B) \) each corresponds to WB settings based on thermal light source of various colour temperature. The square marker indicates \( k \) of white LED effective spectrum white balance settings. The circle points the \( k_{\text{min}} \) values at which minimum value of the coherence function width \( I_{3200, \min} = 2^{7.1} \cdot k_R - 1, k_G = 2^{8.7} \cdot 1.17 \ \mu m \) is achieved. The absolute value and the real part of the summarized coherence function of 3200K light source irradiation, registered with Sony ICX204AK image sensor and appropriate colour balance coefficients are shown on fig. 1b. The gray curves correspond to regular white balance settings and the black ones to \( k_{\text{min}} \).

Fig. 1. The dependence of the summarized coherence function width on white balance settings for the halogen lamp (a) and the function absolute value and real part (b) of the coherence function with color correction being adjusted for white balance (gray curves) and for minimum of the coherence pulse width (black curves)

The summarized coherence functions widths of different sources are presented in Tab. 1. The term \( I_{\min} \) stands for the minimum value of the coherence function width being achieved using Sony ICX204AK (DCU223C Thorlabs colour camera, Germany) image sensor color balance correction where the term \( I_{\text{source}} \) means the value of the coherence function width when the colour balance is adapted to comply with the light source spectrum. To compare we have also calculated FWHM \( I_{\text{mono}} \) in case of using monochrome image sensor Sony ICX204AL (DCU223M camera Thorlabs, Germany).

<table>
<thead>
<tr>
<th>Light source</th>
<th>FWHM of interference pulse</th>
<th>WB coefficients values</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 2000^\circ K )</td>
<td>1.27</td>
<td>( I_{\min} = 1.55 \ \mu m \ (18%) ), ( I_{\text{source}} = 1.45 \ \mu m \ (12%) ), ( I_{\text{mono}} = 1.00 \ \mu m \ (-17%) ), ( \log_2 k_{\text{RGB}} = 3.7; 0; 7.2 )</td>
</tr>
<tr>
<td>( 2800^\circ K )</td>
<td>1.19</td>
<td>( I_{\min} = 1.45 \ \mu m \ (18%) ), ( I_{\text{source}} = 1.31 \ \mu m \ (9%) ), ( I_{\text{mono}} = 1.00 \ \mu m \ (-17%) ), ( \log_2 k_{\text{RGB}} = 5.7; 0; 7.7 )</td>
</tr>
<tr>
<td>( 3200^\circ K )</td>
<td>1.17</td>
<td>( I_{\min} = 1.41 \ \mu m \ (17%) ), ( I_{\text{source}} = 1.41 \ \mu m \ (17%) ), ( I_{\text{mono}} = 1.00 \ \mu m \ (-17%) ), ( \log_2 k_{\text{RGB}} = 7.1; 0; 8.7 )</td>
</tr>
<tr>
<td>WD</td>
<td>1.45</td>
<td>( I_{\min} = 1.66 \ \mu m \ (12%) ), ( I_{\text{source}} = 1.82 \ \mu m \ (20%) ), ( I_{\text{mono}} = 1.00 \ \mu m \ (-17%) ), ( \log_2 k_{\text{RGB}} = 5.3; 0; 4.5 )</td>
</tr>
</tbody>
</table>

4. Conclusion
The results show that the minimum interference pulse width can be achieved by the proper white balance coefficients choice. And in this case the pulse is narrower than either one registered by colour image sensor with WB based on light source color temperature or by monochrome image sensor (Tab. Fehler! Verweisquelle konnte nicht gefunden werden.). In addition since the usage of colour image sensor reduces the spectral range and the restrictions on optical components quality decline as well.

References
PULSED LASER NANOSTRUCTURING, ASSEMBLING AND IMMobilизации OF LEVAN AND IgG

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Laser-assisted methods prove some key advantages over the other deposition techniques: the accurate control of the layer thickness and/or expelled material, absence of contamination, uniform distribution of material over quite large areas and rather easy synthesis of multistructures. Matrix Assisted Pulsed Laser Evaporation (MAPLE) method was particularly developed to provide a soft laser transfer of organic and/or biologic materials. Extremophilic microorganisms provide non-pathogenic products, suitable for uses in food industry, pharmacy and cosmetics as emulsifiers, stabilizers, gel agents, coagulants, thickeners and suspending agents. One exopolisaccharide (EPS) extremophile producer is the halophilic Halomonas sp. AAD6 bacteria, which secrets high level of levan. Immunoglobulins (Ig) are gamma globulin proteins present in blood or other bodily fluids of vertebrates and used by the immune system to identify and neutralize bacteria and viruses. IgG is the only isotype that can pass through the human placenta, providing protection to the fetus in utero. It can bind to many kinds of pathogens, and protects the body by agglutination and immobilization.

The protein immobilization depends on composition, reactivity, wettability, and roughness of the substrate surface. Special attention is paid to adhesion and stability of the layers. Functionality of the structures is proved by immunostaining assays.

IgG transfer by MAPLE

We previously reported [1] the sheltered transfer and immobilization of rabbit anti-human antiserum immunoglobulin G (IgG) by Matrix Assisted Pulsed Laser Evaporation. The iced targets submitted to laser irradiation consisted of (0.2 – 2) mg/ml IgG blended or not with lipid (L-α-phosphatidylcholine dipalmitoyl) dissolved in distilled water based saline buffer. Thin IgG coatings were obtained at room temperature onto glass, fused silica or silicon substrates. Ten thousand subsequent laser pulses of 0.33, 0.5 or 0.67 J/cm² fluence were applied for the synthesis of each sample. Morphology and composition of the thin films were studied by optical, scanning and atomic force microscopy and Fourier transformed infrared spectrometry. Optical labeling methods such as spectrofluorimetry and fluorescence microscopy were selected to verify the biosensor transduction principle because of their high sensitivity for detecting low amounts of antigen (IgG). Protein immobilization to the substrate surface was demonstrated for all obtained structures after immersion in the donkey anti-rabbit secondary antibody solution. The IgG transfer and immobilization onto substrates was improved by addition of lipid to MAPLE solutions. There is however a “window” in laser fluence (~ 0.5 J/cm²) for which the integer structure of the protein was preserved and morphology can be well controlled. A larger amount of protein was detected in structures...
deposited on fused silica. The tunable approach of all parameters could be essential in developing a performant immunosensors for versatile applications.

**Exopolisacharides transferred by MAPLE**

The transfer of pure levan and oxidized levan by MAPLE was achieved without any addition of plasticizers or pigments [2]. We mention that the deposition of this delicate biomaterial was unapproachable by any other laser or other techniques. The coatings preserved the bulk composition as demonstrated by the IR absorption data. The samples presented a compact structure, good adhesion to substrate and a uniform, homogenous nanostructured surface. They exhibited high specific surface areas fully compatible with their potential use in biology or medicine. Cell viability and proliferation studies confirmed the biocompatible behavior of the synthesized nanostructures. The oxidized levan thin films induced an increase in cell proliferation as compared with the simple levan coatings. This result is in good agreement with the contact angle data which evidenced a higher hydrophilicity in case of oxidized levan samples which was assigned to the acidic aldehyde-hydrogen bonds forming after oxidation.

We report herewith the fabrication of simple and multi-layered structures of IgG and EPS by laser transfer methods on Si wafers. Our aim was to promote a better immobilization of the protein, without the use of any other additives, like lipids. Morphological and compositional characterization was performed by optical, atomic force and scanning electron microscopy. Fourier transform infrared (FTIR) spectrometry investigations and AIM-FTIR mapping using an IR microscope for compositional distribution were carried out. We observed that the coatings preserved the bulk composition, presented a compact structure, good adhesion to substrate and a uniform, homogenous nanostructured surface. They exhibited high specific surface areas fully compatible with potential use in biology or medicine. The biocompatible behavior of the synthesized nanostructures was confirmed by cell viability and proliferation studies.

**References**


To achieve power scaling beyond 25kW, interferometrically combining multiple laser beams is appealing since it is reminiscent of modern phased-array conformal radars allowing for electronic beam control. The basic building block of such an architecture is the master-oscillator-power-amplifier (MOPA) subsystem based on amplification in optical fiber. High-power optical-fiber amplifiers are outstanding brightness enhancing devices since they achieve nearly ideal beam quality with excellent electrical-to-optical power conversion efficiency. Unfortunately, increasing the power transmission of optical fibers is challenging due to a nonlinear optical effect known as stimulated Brillouin scattering (SBS). The highest powers achieved to date in commercial fiber MOPA systems are in the 1kW range with single frequency master-oscillators broadened to 10GHz bandwidths and 150W with sub-MHz seed sources. We will present two approaches for improving performance by reducing the impact of SBS. The first approach involves sophisticated fiber designs based on careful materials characterization of optical fibers and preforms. The second approach looks at digital modulation formats of the master-oscillator allowing for two-fold improvements at the 1kW level.

1. Introduction

Fiber Lasers are particularly attractive because of their good beam quality in addition to the ability to easily transport optical power, mostly avoiding the need for cumbersome and expensive free space optics. While fiber laser power has seen remarkable increases associated with improvement in optical brightness and electrical-to-optical efficiency of the diode laser pumps, the conventional state of understanding indicates that with current technology single spatial-mode operation per fiber will be limited to ~10 kW. In addition, if single spectral-mode operation is required, the best results shown to date have achieved 1.5 kW of optical power at the expense of large frequency bandwidth, ~10GHz. Single frequency is indeed an additional ingredient required to achieve two important additional functions for future systems: a) The ability to coherently, i.e. interferometrically, combine multiple fiber lasers allowing for power scaling only limited by Size and Weight constraints of the system and b) Electronically steer and control the output beam of the laser system. These two functionalities will be highly desirable and ultimately are expected to be key to practical and operationally maintainable high power laser systems for long range power projection.

Unfortunately, it has been known since the 1970s that increasing the power transmission of optical fibers is challenging due to a nonlinear optical effect known as stimulated Brillouin-scattering (SBS). This effect is a power limiting effect, resulting in optical power being reflected back along the optical fiber while power is increased. The effect is stochastic in nature and is initiated by thermal fluctuations along passive fibers and also by backward propagating spontaneous emission in fiber amplifiers.

1.1 Digital Phase Modulation achieving reduced bandwidth at 1kW

The interaction between two optical counter-propagating fields and a longitudinal phonon can be derived from first principles and is well represented by the following set of nonlinearly coupled differential equations:

\[
\frac{\partial E^S}{\partial z} - \frac{1}{v_g} \frac{\partial E^S}{\partial t} = (g(z, t) - \alpha_s)E^S - g_0 Q E^B + ik_s n_1 \left( |E^S|^2 + 2 |E^B|^2 \right) E^S \\
\frac{\partial E^B}{\partial z} + \frac{1}{v_g} \frac{\partial E^B}{\partial t} = -(g(z, t) - \alpha_s)E^S - g_0 Q E^S - ik_s n_1 \left( |E^S|^2 + 2 |E^B|^2 \right) E^B \\
\frac{\partial Q}{\partial t} + \frac{Q}{\tau_g} = g_0 E^S E^B \ast + N^Q
\]

Eq. 1-a,b,c

Where \( E^S \) and \( E^B \) represent the complex amplitude forward propagating signal and backward propagating scattering wave and \( Q \) represents the magnitude of the acoustic-phonon mode. \( N^Q \) represents the stochastic
thermal fluctuation or spontaneous emission starting/seeding the SBS process. The optical gain \( g(z,t) \) in a fiber amplifier and is found separately by solving the rate equations associated with the amplifier. The intrinsic optical losses \( \alpha \) in the fiber and are typically neglected for the lengths of interest. Material constants, \( g^1 \) and \( g^2 \) are the two phonon-photon coupling coefficients and \( n_2 \) is the nonlinear optical Kerr coefficient. It assumes that \( E^S \) and \( E^B \) are monochromatic, in other words the linewidth of the electromagnetic fields is narrower than the spontaneous acoustic linewidth of the phonon resonance \( \sim 1/\tau_B \).

In steady state or long time scales \( (d/dt<<1/\tau_B) \), one can easily show that SBS is a phase-matched process. In other words, the phase relation between the two optical fields does not play any role. The back propagated power, in the low depletion approximation is equal to the incoherent sum of all the stokes shifted waves, denoted by \( \nu \), with an exponential gain proportional to the forward propagating laser power \( P_L \) and proportional to the overlap between optical and acoustic modes supported by the waveguide structure in the fiber.

\[
P_{\text{Stokes}}^B = \sum_{\nu} P_{\text{Stokes}}(z = 0) \exp\{\int_0^{L_F} g_{\nu}(\nu,z)P_L(z) \, dz\} \quad \text{Eq. 2}
\]

However, if the complex optical fields vary rapidly compared to the decay of the optical phonon, the amplitude \( Q \) of the guided optical phonon, stores/integrates the information of the difference in phases between the forward and the backward propagating optical waveguide modes. In this regime, the process is not automatically phase matched! Our proposed approach takes advantage of this fact to reduce the effect of SBS when the phase of the signal is modulated at frequencies higher than the inverse of the phonon-lifetime, i.e. >>50MHZ.

\[
\Delta Q(z,t) = \left[ g_{\nu}^2 \int_0^{L_F} E^S(z,t') \left( E^B(z,t') \right) e^{i\nu t'} dt' \right] e^{-i\nu t} \quad \text{Eq. 3}
\]

We have numerically integrated the nonlinearly coupled Eq.1-a,b,c in the case of a well characterized pump probe numerical experiment. We have assumed a constant counter-propagating wave in resonance with the acoustic phonon and the forward propagating signal in a passive fiber. Two cases have thus far been investigated:

- On the left side of Figure 1 we show the amplification due to SBS observed by the counter-propagating probe when the forward pump has a constant phase.
- On the right side of Figure 1 we show the reduced gain when the phase periodically alternates from 0 to \( \pi \).

Note the significant reduction in SBS gain in this case.

### 1.2 Design of Acoustic profiles in High-Power-Fiber-Optics for SBS mitigation

We have investigated a parallel approach optimizing the acoustic profile of large core optical fibers to reduce the effects of SBS. This strategy results from Eq.2, note the index \( \nu \) referring to the SBS-Stokes shift associated with a longitudinal acoustic mode of the fiber. An engineered core can manipulate the SBS gain spectrum, represented by the sum over all acoustic modes in Eq. 2, and thus reducing the overall peak SBS gain. Examples of our design methodology will be presented at the meeting in addition to some of our experimental characterization performed on both preforms and large core optical fibers.
DYNAMICS OF FEMTOSECOND LASER INTERACTION WITH DIELECTRICS AND SEMI-CONDUCTORS

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Abstract: Dynamics of femtosecond laser interaction with fused silica and silicon is studied. Experiments based on pump-pump and pump-probe setups are carried out associated to theoretical models describe the physical mechanisms and the main experimental parameters involved in the energy absorption of femtosecond laser pulses of transparent materials. To analyze transparent materials, we consider the interaction of fused silica at 1030 nm and 800 nm and of silicon at 1.3 µm. Due to non-linear absorption and for specific conditions, the energy deposition can be optimized and confined in the micro-scale and sub-micro-scale regions for both materials. The results are particularly relevant to high precision 2D and 3D laser micromachining.

1. Introduction

Efficient use of lasers for material processing at submicron scale requires a deep knowledge of complex phenomena such as carrier excitation, thermalization, carrier removal, thermal and structural effects governing the interaction of laser radiation with matter and the mechanisms of laser ablation. For this goal, numerous experimental and theoretical studies of laser–matter interaction have been carried out by many researchers [1]. Considering femtosecond laser interaction with dielectrics and semiconductors, the laser field excites the electrons from valence to conduction band by two phenomena: photoionization (including multiphoton ionization and tunnel effect) followed by Joule heating and avalanche (impact) ionization. The laser energy deposition in the material is a highly non-equilibrium process, meaning that the free electron plasma is "hot" and lattice is "cold" or "frozen" during laser–matter interaction (Te ≫ Ti).

In order to gain deeper insights of mechanism of laser-matter interaction and ablation dynamics in femtosecond regime, the present talk will be focused on the precise determination of the balance of energy deposition of femtosecond lasers of relatively long pulse duration (500 fs) with dielectrics. The results obtained with long duration (500 fs) pulses will be compared to the situation encountered with ultrashort femtosecond laser pulses (< 10 fs). Then preliminary investigation of infrared (1.3 µm) laser interaction inside semi-conductors (silicon being totally transparent at 1.3 µm) will be presented.

2. Laser interaction with dielectrics

Experimental and theoretical studies of the very first stage of femtosecond laser interaction including laser ionization, energy deposition and its redistribution to the lattice for different interaction regimes (laser damage threshold, laser ablation threshold, and high intensity laser interaction) will be presented and discussed. In particular the energy balance and dynamics in a fused silica sample irradiated by a single femtosecond laser pulse will be considered performing both beam depletion and pump-probe experiments.

Beam depletion yields information concerning the "efficiency" of the laser energy deposition inside material, resulting from the competition between fast ionization and the onset and magnitude of the plasma mirror effect. Measurements of transmission and reflection of the laser beam thus enable to establish the total energy balance and the fraction of incident energy deposited into the material as a function of the incident laser fluence as illustrated by figure 1.

Figure 1: Experimental curves of reflection, transmission and absorption as a function of normalized fluence with respect to the damage threshold F_{th} for a fused silica simple irradiated with a 500 fs single laser pulse at 1030 nm.
These experiments supported by theoretical estimations give information concerning i) the minimal energy to be deposited for transforming the transparent dielectric into an absorbing medium and further for reaching the ablation threshold and ii) the minimal energy for inducing a reflecting medium (self-generation of ultrasfast optical shutter or also called plasma mirror effect).

To obtain additional information on dynamics of absorption and energy deposition in dielectrics, results of careful pump-probe experiments for a wide range of laser fluences will also be presented. Figure 2 give an example of such dynamic experimental data.

![Figure 2](image_url)

**Figure 2:** Experimental evolution of reflected (a) and transmitted (b) energy as a function of pump-probe delay for a fused silica sample irradiated with a 500 fs single laser pulse at 1030 nm.

The interpretation of experimental and modeling results will then open a discussion on the minimal time needed and minimal energy to be deposited to create a highly absorbing medium from an initially transparent material and/or to establish a medium possessing highly reflecting metal-like properties. Influence of incident laser fluence on dynamics of absorption, on the time delay to create a highly absorbing material or a plasma mirror will be also presented. Finally we will show that ablation of dielectrics by a sub-picosecond laser pulse is the result of two phenomena: i) the so-called Coulomb explosion or electrostatic ablation which is responsible for ablation of the depth of several nanometers, this effect occurring rapidly after the end of the pulse, and ii) thermo-mechanical effects occurring on longer time scales and yielding the main part of ablated depth (up to hundreds of nanometers).

The study of laser energy deposition also shows that there is an optimal regime (in terms of a range of fluence maximizing the material removal, expressed in $\text{µm}^3/\mu\text{J}$) yielding high efficiency and control of energy deposition and laser ablation [2]. These results will be related to the final result of ablation (crater depth and volume) measured by atomic force microscopy and compared to much shorter femtosecond pulses (<10 fs).

### 3. Laser interaction with silicon

The origin and localization of non-linear absorption occurring when a femtosecond laser pulse is tightly focused inside n-type doped silicon is investigated. An OPA femtosecond laser system allows working in the infrared domain where the optical radiation energy is below the band gap energy of silicon. At 1.3µm, intrinsic and low-doped silicon substrates are fully transparent to low light intensity like silica irradiated at 800 nm or 1030 nm. With focused nanojoule femtosecond pulses, the intensity in the focal region is sufficient to initiate non-linear absorption. We measure and characterize transmitted pulses interacting with silicon wafers of several doping concentrations. Interestingly, we find the non-linear contribution in absorption does not depend on initial concentration of free-electrons up to $10^{16}.\text{cm}^{-3}$ as it would be predicted with an important contribution of avalanche ionization [3]. To confirm the independence of the non-linear absorption to free-carrier initially present, we perform a double-pulse experiment where a pre-pulse populate the conduction band and we compare the second transmitted pulse to a typical single pulse experiment. We also perform Z-scan experiments to locate the energy deposition in the substrates. Under specific conditions, we find the energy deposition can remain confined in a micron-scale focal region. Our results open a way for 3D microfabrication inside various semiconductor materials by mid-IR femtosecond pulses.

### References


Micro-optics describes a family of elements and systems fabricated by modern micromachining. Optical structures with nearly arbitrary shapes and dimensions down to the nanometer can be realized offering a large degree of freedom for the design. The progress in novel light sources, detectors, materials and technology enable new opportunities and challenges for micro-optics and nanoscale photonics.

1. Introduction

The history of micro-optics is the history of micro-fabrication of fine structures. At the beginning, the elements were simple grating structures for spectroscopy. Then, the elements became more complex. Fresnel zone plates, computer-generated holograms (CGHs), diffractive optics, microlens arrays and more recently resonant filters and photonic crystals are such elements [1-3]. With the improvement of available technology new devices and systems were proposed. The possibility to realize very small structures opened also the door to new materials. Interesting are not only static, but also dynamic elements.

The progress in the field is driven by opportunities, such as the design freedom (diffusers and beam-shaping elements), technology (nanophotonics, plasmonics), new light sources (white light sources, mid-IR lasers, frequency comb lasers), needs (parallel systems to increase the measuring speed), curiosity (negative index materials), standard platform, characterization tools, etc. A few examples will be summarized here.

2. Challenges

2.1 Design freedom - diffusers

Many years have been passed between the invention of CGHs [4] and beam shaping with plasmonic nanostructures [5]. The technique is more powerful, the features are smaller enabling a higher degree of freedom. Amplitude, phase and polarization information can be stored in planar devices and used to control the propagation of light. However, most practical applications require loss-free phase elements. For the application in illumination systems often a space-invariant response of the diffuser is required. The utilization of arrays of microlenses with adapted geometry is straightforward for this application. The lenses generate the desired angular spectrum, while the array property warrants the space invariance of the element. To use diffractive optics or CGHs has the advantage of higher flexibility for arbitrary structures. Such elements are key in illumination systems in DUV-lithography steppers [7]. A design example is shown in Fig. 1. Note that the fabrication tolerances can be improved considerably by an optimized design.

2.2 Technology - sensors

Optical sensors based on refractive index detection are attractive, because they show a high sensitivity and provide a label-free method [8]. The two most commonly used techniques are optical fiber based sensors and surface plasmon resonance technique based sensors. The progress in technology allows the realization of sensors that are able to probe extremely small volumes. However, decreasing the size of the sensor means decreasing its sensitivity proportionally to the interaction strength between light and analyte. Thus a compromise between the size of the sensor and the sensitivity has to be found. In order to study integrated sensors that can probe extremely small analyte volumes [9], metallic cavities with a slot width of 30 nm have been realized on top of a silicon waveguide (see Fig. 2). Simulations show that these devices can be used as sensors with a sensitivity of 750 nm/RIU (refractive index unit). A detailed analysis shows that an optimum resolution down to 5.8 x 10^{-5} RIU can be expected. These are extraordinary results for such small cavities, which are able to probe picoliter volumes.

2.3 New light sources – mid IR

Not only micromachining, but also devices and applications are important factors for the development of new domains. Quantum cascade lasers, for example, are compact light sources working in the mid-infrared (mid-IR) [10]. They are ideal light sources for sensor applications, because most of optical absorption spectral lines associated to the vibrational frequencies of gas molecules take place in the mid-IR domain of the optical spectrum. Mid-IR lasers offer also opportunities for diffractive optics, because the longer wavelength (compared to the visible spectrum) facilitates the fabrication of diffractive structures. Highly efficient binary sub-wavelength structures become attractive and feasible. Mid-IR photonics also needs low-loss integrated waveguides. A germanium strip waveguide on a silicon substrate has been demonstrated recently, see Fig. 3 [11]. The waveguide is designed for single mode transmission of light in TM-polarization generated from quantum cascade lasers at the wavelength of 5.8 μm. The propagation losses were measured with the Fabry- Pérot resonance method. The lowest achieved propagation loss is 2.5 dB/cm.
2.4 Standard platform – Bloch Surface Waves (BSWs)

The concept of Bloch Surface Waves (BSWs) in periodic layered media has been studied first by Yeh et al. in 1978 [12]. It has been shown that truncated dielectric multilayers can sustain surface waves under particular illumination conditions. Recently it has also been shown by Descrovi et al. [13] that these waves may be guided thanks to a dielectric waveguide on top of the multilayer. Finally, Sfez et al. [14] demonstrated the refraction of surface waves at thin waveguide structures, which opens the door for a novel 2D-platform. Different types of thin optical elements (lenses, gratings, cavities, nanostructures, …) can be arranged on the surface to realize optical systems for sensing applications. Therefore, the dielectric multiplayer is an ideal platform for 2D integrated optics.

BSWs have several interesting advantages. The dielectric materials can be chosen with very low intrinsic losses for a specific wavelength. The multilayer is wavelength scalable, i.e., the structure may be designed to sustain BSWs at any wavelength. It is possible to engineer the position of the surface mode within the forbidden bandgap. Finally, the multilayer fabrication is fully compatible with the actual fabrication technologies.

3. Conclusion

The success of micro-optics is based on the progress in wafer-scale fabrication methods. The high degree of freedom offers a wide range of possibilities that have not yet been fully explored. The progress in novel light sources, detectors, materials and technology enable new opportunities and challenges for micro-optics and nanoscale photonics.

References
Cr$^{4+}$-doped materials attract a significant attention as the active media of femtosecond and tunable solid state lasers, emitting in the wavelengths range of 1.2 – 1.6 μm. Development of new efficient laser hosts for Cr$^{4+}$ still remains the important and unsolved problem. Transparent Cr$^{4+}$:LiGaSiO$_4$ nano-glass-ceramics is one of the most promising new materials for Cr$^{4+}$ solid-state lasers. The talk reports the study of main spectroscopic characteristics of the transparent Cr$^{4+}$:LiGaSiO$_4$ nano-glass-ceramics, and of the vitreous Cr-Li-Ga-Si-O precursors. Chromium is present mainly as Cr$^{3+}$ and Cr$^{6+}$ in the vitreous precursors. Peak cross-sections of the characteristic Cr$^{3+}$ and Cr$^{6+}$ absorption bands were evaluated. Based on these values, the actual concentrations of Cr$^{3+}$ and Cr$^{6+}$ in the samples were calculated. The total actual Cr contents in our samples appeared to vary from 2% up to 60% of the initially introduced ones, depending on the charge compositions and on the synthesis regimes. During ceramming of the samples chromium transforms into tetravalent state. Strong optical absorption bands of Cr$^{4+}$ appear, whereas the absorption bands of Cr$^{3+}$ and Cr$^{6+}$ simultaneously reduce. The fluorescence excitation spectra of the cerammed samples reproduce the novel appeared Cr$^{4+}$ absorption bands in a great extent. The emission of two non-equivalent Cr$^{4+}$ centers appears, corresponding to the dopant ions located in the α-LiGaSiO$_4$ and in the γ-LiGaSiO$_4$ crystalline polymorphs. The lifetimes of these two centers drastically differ from each other, while the fluorescence spectra (bandshapes, peak positions, and linewidths) are very similar.

Cr$^{4+}$-doped materials attract a significant attention as the active media of femtosecond and tunable solid state lasers emitting in telecommunication and eye-safe wavelengths range of 1.2 – 1.6 μm. The main problem, inhibiting the wide application of Cr$^{4+}$-lasers is the absence of efficient hosts for this ion. YAG and forsterite single crystals used up to now as the hosts for Cr$^{4+}$, as well as Cr$^{4+}$-doped glasses possess rather low fluorescence quantum efficiency due to strong multiphonon non-radiative relaxation of the excited state [1-4]. Moreover, it is impossible to reach high enough concentrations of Cr$^{4+}$ ions in these materials [5-6]. Other single crystals, with higher Cr$^{4+}$ admittance, better fluorescence quantum efficiency (Ca$_2$GeO$_4$, Li$_2$ZnSiO$_4$, LiAlO$_2$, LiGaSiO$_4$, etc.) can hardly be grown as high-quality bulk samples. Besides that, there are some problems with fitting the single-crystalline active media with optical fibers. This problem can be solved by using Cr$^{4+}$-doped nano-glass-ceramics, which, like glasses, can be fabricated fabricated with use of relatively simple techniques in any shapes, including single-mode waveguides [7]. This kind of materials, consisting of fine-grained crystallites dispersed in a residual vitreous phase, is good alternative to single-crystalline laser media, when fabrication of the latter ones is challenging. Usually nano-glass-ceramics reproduce the spectroscopic properties of the corresponding single crystals in a high extent.

During the last decade Cr$^{4+}$-doped nano-glass-ceramics attract very big interest as promising laser media [3, 4, 7, etc.]. However, laser action at these materials has not been achieved so far, to our knowledge. Broadband optical amplification at Li$_2$ZnSiO$_4$:Cr$^{4+}$ nano-glass-ceramic has only been reported with the gain coefficient of 1.27 cm$^{-1}$ [7]. This report is devoted to the investigation of the main spectroscopic characteristics of Cr$^{4+}$:LiGaSiO$_4$ nano-glass-ceramic [8, 9], as well as of the vitreous Cr-Li-Ga-Si-O precursors of different compositions. Transparent vitreous precursors were made by standard melt-and-quench technique in air, and in the inert atmosphere. Partial ceramming of the precursors was reached by their additional annealing at the special thermal-temporal regimes.

According to the spectroscopic data, chromium coexists mainly as Cr$^{3+}$ and Cr$^{6+}$ in the vitreous precursors, with minor amounts of Cr$^{4+}$, see fig. 1a. Peak cross-sections of the Cr$^{3+}$ and Cr$^{6+}$ absorption bands were evaluated to be: \( \sigma(Cr^{3+}) = (2,40\pm0,05)*10^{-19} \text{ cm}^2 \) for the \( ^2\!A_2 \rightarrow ^2\!T_1 \) absorption band at \( \lambda_{\text{max}}=435 \text{ nm (2,3}\times10^4 \text{ cm}^{-1} \); \( \sigma(Cr^{6+}) = (1,0\pm0,2)*10^{-17} \text{ cm}^2 \) for the charge transition band at \( \lambda_{\text{max}}=370 \text{ nm. Based on these values, the actual contents of Cr$^{3+}$ and Cr$^{6+}$ in the precursors were calculated and compared with the Cr concentrations in the initial charges. The actual Cr contents in our samples were found to vary in the range of (0,3-3)*10$^{-19}$ cm$^3$, or from 2% up to 60% of that introduced into the charge, depending on the charge composition, and on the melting duration. The rest chromium, apparently, evaporates from the melt during the glass synthesis. The fraction of Cr$^{3+}$ in the vitreous precursors varies from 77 to 94% of the total chromium content, while the fraction of Cr$^{4+}$ varies from 0 up to 2%. The rest chromium in the precursors is Cr$^{6+}$.

During the partial ceramming chromium transforms into tetravalent state. Strong absorption bands appear, typical for Cr$^{4+}$ ions in crystalline hosts, and corresponding to the orbitally split \( ^2\!A_2 \rightarrow ^2\!T_1 \text{ and } ^2\!A_2 \rightarrow ^2\!T_2 \) vibronic transitions, see fig. 1b. Despite of strong overlapping, at least four maxima of this absorption at ~ 585, 660, 755 and 950 nm are clearly seen. At the same time, the absorption bands of Cr$^{3+}$ and Cr$^{6+}$, located in the vitreous phase, simultaneously reduce. The emission of only Cr$^{3+}$, peaking at 935 nm, is observable in the vitreous precursors at 300K, although at 77K rather
weak Cr$^{4+}$ emission, peaking at 1.12 µm, also appears. After ceramming the intensity of NIR emission drastically increases. Peak position of the emission shifts to ~1280 nm, see fig. 2. The fluorescence excitation spectrum of the cerammed samples at 300K (monitoring of the emission signal was performed at 1350 nm) reproduce the novel appeared absorption bands in a great extent. This indicates that the absorption bands seen in the fig. 1b (magenta colored lines), correspond to the Cr$^{4+}$ ions located in the crystallites, not in the residual glass. Cr$^{4+}$ fluorescence of the Cr:LiGaSiO$_4$ nano-glass-ceramics has double-exponential decay kinetics at both 77, and 300K, indicating that there are two kinds of the Cr$^{4+}$ luminescent centers. These two centres were earlier found to correspond to the Cr$^{2+}$ ions located in the α-LiGaSiO$_4$ and in the γ-LiGaSiO$_4$ crystalline polymorphs. The decay times of these two centers are 12 and 2 µsec respectively at 300K. Thus, the probabilities of the radiative, and, perhaps, of the non-radiative excited state relaxations are quite different in these two kinds of the luminescent centers. This can be related with different sets of the active phonon modes, promoting the relaxations.

Meanwhile, the emission spectra of the samples, containing the crystallites of only α-LiGaSiO$_4$:Cr, and of only γ-LiGaSiO$_4$:Cr polymorphs separately, are looking very similar, see fig. 2.

They have very close bandshapes, fluorescence ranges, peak positions and FWHMs. It means, that the crystal field strength and symmetry at Cr$^{3+}$ ion in these two hosts are very similar, despite the pronounced differences of the structures of α- and γ-LiGaSiO$_4$ in general. FWHM of the emission band is about 300 nm that gives hope to obtain the laser action tunable in a very broad range. The lifetime of 12 µsec for α-LiGaSiO$_4$:Cr$^{4+}$ nano glass ceramics is close to that for LiGaSiO$_4$:Cr$^{4+}$ single crystals [10], and by factor of 3 longer than that for Cr$^{4+}$:YAG [1], that can indicate the increased fluorescence quantum efficiency of α-LiGaSiO$_4$:Cr$^{4+}$ nano glass ceramics.

Besides that, the emission of Cr$^{3+}$ in the residual glass is also seen at the shorter-wavelength part of the fig. 2.

References
NOVEL RARE-EARTH DOPED GLASSES FOR INFRARED LASERS

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We present a review of recent research in the field of novel material engineering for lasers in the 1.5 – 4 µm range. Tellurite and germanate glasses doped with Tm³⁺ and Ho³⁺ have been utilized to produce CW, Q-switched and fs fiber and bulk glass lasers operating in the 2 µm wavelength region. Tellurite glasses doped with Dy³⁺ have been shown to exhibit broad fluorescence in the 3 – 4 µm range and may form promising hosts for future mid-IR lasers.

1. Introduction

Tellurite (TeO₂) and germanate (GeO₂) glasses have been studied for their spectroscopic and laser properties which offer advantages over other common glass hosts such as silica and ZBLAN. Tellurite glass has a low phonon energy for an oxide glass of ~700 cm⁻¹ compared to 1100 cm⁻¹ for silica which allows transmission further into the infrared (up to around 5 µm), and results in higher radiative rates and lower non-radiative rates of rare-earth ions doped into the glass. Compared to ZBLAN glass, tellurite is more thermally, environmentally and chemically stable allowing more robust devices to be constructed. Tellurite glass is unique that is made up of different structural units, namely TeO₄ bipyramid and TeO₃ pyramid and TeO₃⁺⁺ polyhedron, and these result in different Te-O bond lengths and a greater variation in crystal field strengths experienced by the rare-earth ion dopants. This generally results in broader spontaneous emission linewidths in tellurite glass which can be beneficial for laser tunability and for short pulse generation through mode-locking. While having a slightly higher phonon energy than tellurite glass of 980 cm⁻¹, germanate glasses are robust, strong glasses suitable for laser research in the ~2 µm wavelength region.

1.1 Experimental techniques

Tellurite glass is fabricated using standard melt quenching techniques to form either bulk samples by casting into appropriate moulds, or fiber preforms using suction and rotation casting [1]. Tm³⁺/Ho³⁺ tellurite fiber lasers were pumped using diode-pumped silica fiber lasers, doped with either Yb³⁺ or Er³⁺/Yb³⁺ for operation at 1.1 µm and 1.6 µm, respectively. Fiber laser performance with respect to pump wavelength, fiber length and output coupler reflectivities were investigated. Figure 1 shows a schematic diagram of the fiber laser experimental set-up. Bulk Tm³⁺ and Ho³⁺ doped tellurite and germanate glass lasers were characterized for laser bandwidth and fs mode-locked operation. The mid-IR fluorescence of a range of Dy³⁺ doped tellurite bulk glass samples were measured using an Edinburgh Instruments FLS920 Steady-State and Time-Resolved Fluorescence Spectrometer fitted with a liquid nitrogen cooled InSb photodetector.

Figure 1: Schematic diagram of the experimental set-up for the CW fiber laser experiments.
2. Results

2.1 Tm$^{3+}$/Ho$^{3+}$ tellurite fiber laser

By in-band pumping of Tm$^{3+}$ using a 1.6 $\mu$m Er$^{3+}$/Yb$^{3+}$ silica fiber laser, it was possible to achieve a slope efficiency of 76% from a 2 $\mu$m Tm$^{3+}$ doped tellurite fiber laser with a maximum (pump limited) output power of 280 mW. Figures 2 a) and b) show the output power with respect to pump power and laser output spectrum, respectively [2].

When the same 1.6 $\mu$m pump source to pump a Tm$^{3+}$/Ho$^{3+}$ tellurite fiber laser, 2.1 $\mu$m laser output with a slope efficiency of 62% and maximum (pump limited) output power of 160 mW was achieved. This laser was also actively Q-switched using a chopper to produce 100 ns long pulses of 0.65 $\mu$J from a non-optimized set-up. Figure 3 a) shows the 2.1 $\mu$m output power with respect to pump power and figure 3 b) shows the Q-switched pulse train [3].

2.2 Tm$^{3+}$/Ho$^{3+}$ bulk tellurite and germanate glass laser

Following on from the demonstration of tellurite fiber lasers operating in the 2 $\mu$m wavelength band, CW and mode-locked lasers have been demonstrated using Tm$^{3+}$ and Ho$^{3+}$ doped tellurite and germanate bulk glasses using 790 nm diode lasers and 1212 nm semiconductor disc laser pump sources. These results are reviewed and discussed.

2.3 Mid-IR tellurite glass spectroscopy

Beyond 2 $\mu$m, there is great interest in laser devices operating in the mid-IR region of 3-5 $\mu$m where there is an atmospheric transmission window. Current solid-state lasers operating in this region typically use fluoride based materials which are generally not very robust. The fluorescence spectroscopy of Dy$^{3+}$-doped tellurite bulk glasses show mid-IR fluorescence extending up to ~4 $\mu$m compared to 3 $\mu$m in ZBLAN glass. The results and implications for new mid-IR laser devices are presented and discussed.

References
After the successful demonstration of the first laser in the early 60s it took another two decades until the first applications in 2D sheet metal cutting were performed. A rapid development followed, where the huge potential of CO2-gas lasers entered more and more industrial applications. A high degree of industrial maturity was reached soon and new developments lead to increase of power to multiple kilo-watts and improve of beam quality with power densities in the range of 10MW/cm². With such laser tools sheet metal cutting of several tens of millimeters is possible. During the last years the speed of innovation slowed down for the CO2 gas laser and the fiber laser appeared on the horizon. During the last 5 years there was a tremendous race to catch up in fiber laser performance compare to CO2 lasers. Today it is clear that the fiber laser will gain significant share of sheet metal cutting market. Due to its wavelength in the 1um range compared to 10um for CO2, the cutting process is different and much higher cutting speeds in thin metal can be realized, leading to higher productivity. But again, another laser type seems to be short before its first industrial readiness – the diode direct laser.
VERSATILE APPLICATIONS OF ULTRAFAST LASERS

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Lasers with femto and picosecond pulse duration find numerous applications from basic research over telecommunication to security and defence. We will highlight a few concepts of amplifier techniques and applications and draw conclusions on the needs of the corresponding laser parameters.

1. Introduction
The commercial availability of robust and reliable ultrafast lasers enabled a wide spread use of their unique properties in a wide application space. Nowadays, ultrafast lasers can cover sub ns pulses down to sub 100 fs pulse duration at various wavelengths, pulse energies and pulse repetition rates. Pulse energies can range from 100’s of pJ, typically provided by mode locked fiber lasers or gain-switched diode lasers (commonly named as “seed” laser), up to micro Joule of even Joule pulse energy after consecutive pulse amplification.

2. Amplification schemes
Over the last decades, various amplification schemes have been developed and brought to market by various companies. One approach is based on scaling the power of the laser oscillator up, so that no additional amplifier is needed and high energy pulses are directly emitted from the oscillator output. This concept works in principle well in the fs and ps regime, however due to the stringent requirements on mode quality and the natural appearance of intracavity non linearities, the concept is currently more prolonged by the academic research groups [1].
A slightly modified concept is based on cavity dumped oscillators, where high energy pulses are extracted from a low-loss oscillator via electro-optic switching. Mode-locking start-up instabilities and the limited extractable pulse energy are limiting factors of this approach [2].
Commonly used concepts for amplification schemes are either based on a master-oscillator-power-amplifier (MOPA) or regenerative amplifier (REGEN) architectures. The REGEN is a very well known technique for many years and very high pulse energies (up to a few ten’s of mJ) can be easily achieved. However, it suffers from rather limited accessible repetition rates (limited to approx 1 MHz) and required high voltages (a few kV) to operate the electro-optic switches. The MOPA is a relatively new concept (wide spread deployment happened during the last 5 years), partly enabled though the development of a new class of active fibers and new design methods for solid-state amplifiers. A low energy seed laser is consequently amplified in various pre amplifiers and power amplifiers to the required power level. The advantage is clearly the flexibility of the pulse repetition rate (maximum is defined by the seed laser only) and it’s straight forward architecture, manufacturability, robustness and potentially low cost approach.

3. Application examples for low and high energy ultrafast lasers
The applications space is constantly growing and most of the applications are currently transforming from an early adopter phase into a wider accepted technology stage. Optical and practical requirements on ultrafast laser sources are often as numerous as the applications itself. The following table shows a brief summary of typical applications and the requirement on the laser source:

<table>
<thead>
<tr>
<th>Application</th>
<th>Energy</th>
<th>Repetition rate</th>
<th>Duration</th>
<th>Wavelength</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-photon microscopy</td>
<td>5 nJ</td>
<td>80 MHz</td>
<td>200 fs</td>
<td>Visible - NIR tunable</td>
</tr>
<tr>
<td>3D lithography</td>
<td>10 nJ</td>
<td>40 MHz</td>
<td>100 fs</td>
<td>Visible</td>
</tr>
<tr>
<td>Optical frequency combs</td>
<td>2 nJ</td>
<td>100 MHz</td>
<td>100 fs</td>
<td>NIR</td>
</tr>
<tr>
<td>Terahertz generation</td>
<td>5 nJ</td>
<td>80 MHz</td>
<td>100 fs</td>
<td>NIR</td>
</tr>
<tr>
<td>Electro optic sampling</td>
<td>10 pJ</td>
<td>1 GHz</td>
<td>1 ps</td>
<td>C-band</td>
</tr>
<tr>
<td>RZ pulse generation</td>
<td>10 pJ</td>
<td>40 GHz</td>
<td>5 ps</td>
<td>C-band</td>
</tr>
<tr>
<td>Optical clock distribution</td>
<td>1 nJ</td>
<td>250 MHz</td>
<td>100 fs</td>
<td>C-band</td>
</tr>
<tr>
<td>Micro machining</td>
<td>100 uJ</td>
<td>500 kHz</td>
<td>10 ps</td>
<td>Visible - NIR</td>
</tr>
<tr>
<td>Medical</td>
<td>50 uJ</td>
<td>100 kHz</td>
<td>500 fs</td>
<td>NIR</td>
</tr>
<tr>
<td>PV production</td>
<td>10 uJ</td>
<td>1 MHz</td>
<td>100 ps</td>
<td>Visible - NIR</td>
</tr>
</tbody>
</table>
As it can be seen, ultrafast laser solutions have to span from low energy pulses at GHz repetition rates in the C-band (1550 nm) to high energy pulses at kHz rep rates in the visible, i.e. more than 70 dB in terms of energy and more than 60 dB in terms of repetition rate. This leads to a big variety of developed lasers and technologies with no common standard or interface specifications. Fragmentation, high expenditure on R&D and limited availability of second source suppliers are among the remaining challenges of the ultrafast laser community.

4. Conclusion

Even though many applications have been identified where ultrafast laser with their unique properties serve as a key enabling technology, demanding requirements on power, pulse duration or pulse energy in combination with low cost expectations and are still hindering a truly pervasive use of these lasers with production volumes exceeding 10’000 units p.a. New concepts, based on a stringent low-cost approach together with innovative packaging and manufacturing concepts could ultimately break this barrier.

References
NEW CIRCULATION SYSTEM OF LASER GAS MIXTURES

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Abstract
The paper describes a gas circulation system on the principal of an electrohydrodynamic flow driving by a high-frequency barrier discharge distributed over the surface of a dielectric. Investigation results of this system are presented. An electric-discharge laser circulation system with a gas flow rate higher than 15 L s^{-1} was proposed.

1. Introduction
To form high velocity gas media, advantage is traditionally taken of different types of mechanical fans with rotating vanes; these fans, however, have several fundamental drawbacks like outer dimensions, weight, form factor, vibrations, noise, etc., which arise from the presence of elements rotating at a high velocity. In electric-discharge lasers, use is made of circulation whose operation relies on the effect of ‘electric wind’. In this systems the gas flow is produced due to a corona gas discharge [1]. A disadvantage of the corona discharge is the existence of the limiting (up to 3 L s^{-1}) value of gas flow rate [1], which limits the application of such systems in high power lasers. An alternative circulation systems on the principal of an electrohydrodynamic (EHD) flow is considered in this work. The feature of such systems is the using of a periodic gas discharge across a dielectric barrier instead of a corona discharge. This discharge serves as the source of ions, which drift in the external electric field and transfer the momentum to neutral gas molecules to produce the EHD flow. The aim of our work is to investigate the feasibility of producing EHD flow rates higher than 10 L s^{-1} for the circulation of gas media in electric-discharge lasers.

2. EHD flow
To analyse experiments, we give several computational characteristics of the EHD flow. We proposed a one-dimensional model describing the ion beam drifting in the external electric field – between a plane-parallel emitter and an ion collector [2,3]. The calculated dependence of the ion current $I$ on the collector voltage $U_0$ is described by the expression

$$I = S \cdot j = \frac{\varepsilon_0 S \cdot \mu \cdot \varepsilon_0 \cdot U_0^2}{d^2}$$

where $S$ is the effective area of the ion emitter; $d$ is the separation between the emitter and the collector; $\mu$ is the ion mobility and $\varepsilon_0$ is the electric constant.

For velocity $V$ of the gas flow we to find

$$V = \sqrt{\frac{\varepsilon_0}{\varepsilon_0 \cdot \rho}} \cdot \frac{U_0}{d}$$

where $E_0 = U_0 / d$ is the average field intensity in the interelectrode gap between an emitter-collector and $\rho$ is the gas density in the gap.

In our experiments use was made of the setup described in detail in Refs [2,3]. The function of charged particle source was fulfilled by the plasma emitter (PE) with a high-frequency barrier discharge induced on it, the discharge being distributed over the dielectric surface. Above the PE was a metal grid with, which served as an ion beam collector. An alternating voltage $U_f = 5 – 12$ kV with a tunable pulse repetition rate $f = 10 – 25$ kHz was applied to the outer electrodes of the plasma emitter. A constant voltage $U_0 = 0 – 22$ kV of positive polarity was applied to the grid.

Figure 1 displays the experimental dependences of the: (a) - average ion beam current $I$ on the collector voltage $U_0$ as well as (b) - velocity $V$ of the gas flow on value $E_0 = U_0 / d$ for different collector – emitter separation $d$. The most important factor which controls the highest pulse repetition rate of an electric-discharge laser is the velocity $V_0$ of the working gas mixture in the discharge gap of the laser. The circulation velocity in its turn is determined by the gas flow rate provided by the circulation system:

$$W = V_0 \cdot S_d = V_0 \cdot h \cdot l$$

where $S_d$ is the flow section area; $h$ is the interelectrode gap of self sustained discharge; and $l$ is the discharge length.
Figure 1. Experimental dependences of the: a) average ion beam current $I$ on the collector voltage $U_0$; b) air flow velocity $V$ on $E_0 = U_0 / d$ for different collector – emitter separation $d$

Figure 2. EHD flow device

Figure 2 displays a device with three tubular plasma emitters made of metal ceramics, which is intended for the circulation of gas mixtures in electric-discharge lasers. This device may be built in the discharge chamber instead of a propeller. In its operation in the air, the flow rate was higher than 15 L s$^{-1}$, which corresponds to a circulation rate $V_d = W/S_d \approx 5$ m s$^{-1}$ in the discharge gap.

**Conclusion**

We have investigated the electrohydrodynamic air flow produced in the ion emission from the plasma of a high-frequency barrier discharge. A new circulation system on the principle of an electrohydrodynamic flow with a gas flow rate of 15 L s$^{-1}$ and a flow velocity higher than 1.6 m s$^{-1}$ was proposed for electric-discharge lasers.

**References**

THE RESONANCE FLUORESCENCE SPECTRA OF N TWO-LEVEL QUANTUM SYSTEMS LOCATED AROUND THE SPHERICAL NANOANTENNA

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We analyze theoretically in detail the modification of the resonance fluorescence spectrum of the two-level atom driving by the monochromatic field in the close proximity of the plasmonic nanostructure (metal sphere). It is shown that one can control this spectrum varying four key parameters, (i) distance between the atom and the nanosphere, (ii) atom's location around the nanosphere, (iii) the radius of the nanosphere, and (iv) polarization of the incident radiation. These parameters affect the local field enhancement and the modification of the radiative decay rate of the atom interacting with the nanosphere, which lead to modification of the resonance fluorescence spectrum of the atom (frequency shift of the satellite lines in the Mollow-type triplet, widths of the lines, the spectrum intensity) by contrast with that one in free space. The permittivity of the metal the nanosphere is made of is also an additional parameter, which defines the nonradiative decay. The latter in combination with other parameters allows to continuously control the transition from resonance fluorescence enhancement to its quenching. The calculation results are generalized to the case of N two-level atoms, distributed around the nanoparticle in the close proximity of its surface. The calculations were performed for different positions of the detector relative to the system nanoparticle-atom(s).

Since the early indication by Sommerfeld and then the pioneering work of Purcell it is well known that the radiative properties of an emitter (specifically, atom, molecule or quantum dot) are strongly modified in the confined geometries [1]. It has been shown that the plasmonic nanostructures work not only as optical antennas converting the incoming radiation to localized energy and vice versa generating spots of significant enhancement of the local field, but also the lifetime of an excited quantum emitter state of the emitter located near the nanostructure is affected by the radiative decay rate due to photon emission and by the nonradiative decay rate due to energy dissipation in the environment and both these rates for atoms and molecules closed to metal surfaces can be enhanced [2,3]. This results in one of the important applications of the nanoplasmonics—using plasmonic nanostructures for amplifying fluorescence (SEF) and Raman scattering (SERS) and single-molecule sensitivity has been achieved experimentally.

Fluorescence studies also demonstrate that the fluorescence of a single quantum emitter in close proximity of a nanostructure results from both excitation of the emitter by the incident field, which is modified by the local environment, and emission of radiation that is modified by the balance of radiative and nonradiative decays. This results in the continuous transition from fluorescence enhancement to fluorescence quenching while varying the distance between the emitter and nanoparticle. Most fluorescence studies of single atom, molecule or quantum dot have been done using spontaneous fluorescence, whereas the resonance fluorescence, which occurs when the quantum emitter is illuminated by the electromagnetic wave with the frequency close to the emitter's resonant frequency, from atoms, molecules or quantum dots in a confined geometry is just at the start [4]. Key advantage of the resonant fluorescence by contrast with the spontaneous one is that the resonance fluorescence exhibits much more information about the system under study, including quantum features of interaction of incoming radiation with the system.

By analogy with the spontaneous fluorescence, resonance atom fluorescence near the plasmonic nanostructure must also be influenced by the modified incident electromagnetic field and by the modified radiation decay rate of the quantum emitter. Moreover, in the case of strong incoming field, when the Rabi frequency is larger than the modified radiation decay rate, the spectrum of the resonance fluorescence of the two-level quantum emitter becomes more enriched and reveals three lines, which positions and widths bring new valuable information about the emitter and the whole system under study [4].

We analyze theoretically in detail the modification of the resonance fluorescence spectrum of the two-level atom driving by the monochromatic field in the close proximity of the plasmonic nanostructure (metal sphere). It is shown that one can control this spectrum varying four key parameters, (i) distance between the atom and the nanosphere, (ii) atom's location around the nanosphere, (iii) the radius of the nanosphere, and (iv) polarization of the incident radiation. These parameters affect the local field enhancement and the modification of the radiative decay rate of the atom interacting with the nanosphere, which lead to modification of the resonance fluorescence spectrum of the atom (frequency shift of the satellite lines in the Mollow-type triplet, widths of the lines, the spectrum intensity) by contrast with that one in free space. The permittivity of the metal the nanosphere is made of is also an additional parameter, which defines the nonradiative decay. The latter in combination with other parameters allows to continuously control...
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References

We will present recent results on generation of extreme ultraviolet (XUV) frequency combs using intracavity high harmonic generation (HHG) and a near-infrared Yb fiber frequency comb source. The 80-W, 154-MHz repetition rate pump laser, along with better understanding of nonlinear plasma dynamics within the enhancement cavity, has enabled record-level HHG yield of >20 µW outcoupled per harmonic down to 50 nm. Recently, we have also demonstrated the comb structure of the high harmonics by resolving atomic argon and neon lines at 82 and 63 nm, respectively, via direct frequency comb spectroscopy. The argon transition linewidth of 10 MHz, limited by residual Doppler broadening, is unprecedented in this spectral region and places a stringent upper limit on the linewidth of individual comb teeth. Finally, we will discuss ongoing investigations of phase coherence utilizing the heterodyne beatnotes between two independent intracavity HHG systems.

1. Introduction

Development of the optical frequency comb at beginning of the century has revolutionized optical metrology and precision spectroscopy due to its ability to provide a precise and direct link between microwave and optical frequencies. A novel application that aims to extend the precision and accuracy obtained in the visible and near-infrared part of the electromagnetic spectrum to the extreme ultraviolet is the generation of XUV frequency combs via intracavity HHG. The basic idea is to leverage both the ultrashort duration of each laser pulse and the exquisite phase coherence of the continuous pulse train by coupling a high power, high repetition rate (>100 MHz) infrared frequency comb into an optical enhancement cavity. At the intracavity focus, the peak intensities reach $10^{13}$-$10^{14}$ W/cm², required to drive the extremely nonlinear HHG process in a noble gas such as xenon, which produces radiation at the harmonics of the driving infrared laser frequency [1,2].

Here, we present recent advances made in our group [3,4,5] in terms of power scaling and phase coherence measurements. Through advances in high-power Yb fiber frequency comb technology [6], and a better understanding of nonlinear plasma dynamics at the focus of the enhancement cavity [4,5], we have been able to generate >200 µW per harmonic, among the highest harmonic yields reported [5,7]. Furthermore, these power levels have enabled us to confirm the comb structure of the generated light via direct frequency comb spectroscopy in argon and neon at 82 and 63 nm, respectively [3]. Currently, the observed linewidth of these transitions are limited by the thermal motion of the atoms and provide only an upper bound on the comb teeth linewidth. To overcome this limitation, we have constructed two independent intracavity HHG sources in order to study the phase coherence directly via the heterodyne beats between the two sources.

With these developments, many promising applications in the XUV ranging from strong field and molecular studies to ultrahigh precision spectroscopy in highly charged ions and nuclear isomer transitions are within grasp.

2. Laser and Intracavity HHG Setup

As shown in Fig. 1a, a high power Yb fiber frequency comb with a repetition frequency of 154 MHz, a center wavelength of 1066 nm, and a pulse duration of 120 fs [6] is coupled into an enhancement cavity with a build up factor of 200. The intracavity average power in excess of 8 kW corresponding to peak intensities approaching $10^{14}$ W/cm² at the focus can be obtained. Xenon or krypton gas is introduced at the intracavity focus formed by two curved mirrors of 10 and 15 cm radii of curvature using a ~100 µm glass nozzle. The generated harmonics are coupled out of the cavity using a hybrid dielectric mirror/XUV grating with ~10% diffraction efficiency in the first order [8].

3. High Harmonic Power Measurements

HHG spectra and average harmonic powers were measured by recording an image of the dispersed harmonic light on a sodium salicylate coated plate, which fluoresces at ~420 nm when irradiated with XUV light. A typical camera image and a vertically integrated HHG spectrum are shown in Fig. 1b and c, respectively. In order to calibrate the absolute average power in each harmonic, the 13th harmonic power was independently monitored using a calibrated Si XUV photodiode coated with an indium filter in order to suppress stray light from other harmonics, as well as the fundamental IR light. The measured outcoupled powers produced using xenon are in excess of 20 µW/harmonic up to the 19th harmonic at 56 nm, corresponding to more than 200 µW/harmonic generated at the focus. Using krypton, we have been able to outcouple up to the 27th harmonic at 39.5 nm with >1 µW of average power [3].
4. Phase Coherence

To demonstrate the comb structure of XUV radiation, we have spectrally resolved the $3s^23p^6 J=0$ to $3s^23p^5d J=1$ electric dipole (E1) transition in argon with an upper state energy of 121,932.8 cm$^{-1}$ (~82 nm), and the $2s^22p^6 J=0$ to $2s^22p^54s J=1$ E1 transition in neon with an upper state energy of 159,534.6 cm$^{-1}$ (~63 nm) via resonance fluorescence spectroscopy. As shown in Fig. 1a, for these measurements either the $13^{th}$ (82 nm) or the $17^{th}$ (63 nm) harmonic were collimated using a toroidal mirror and steered into an interaction region where the XUV light intersected a supersonic atomic beam propagating orthogonal to it. The fluorescence from the argon or neon atoms was detected using a photomultiplier tube with a sodium salicylate coated entrance window.

A scan of a single XUV comb tooth across the Ar transition is shown in Fig. 1d, where the collimation of the atomic beam has been adjusted to reduce the transverse Doppler width to ~10 MHz. Since there is no evidence of comb linewidth contributing to the observed width of the transition, the measurement provides an upper bound for the XUV comb tooth linewidth of less than 10 MHz.

To further test the phase coherence of the XUV comb source, we have constructed two intracavity HHG comb sources. Light from the Yb fiber comb is split with an acousto-optic modulator to produce two near-infrared combs whose carrier envelope offset frequencies, $f_0$, differ by several MHz. These two near-infrared combs excite two independent enhancement cavities to produce XUV combs with $f_0$’s offset from each other. The XUV combs are then combined on a photodetector to produce beat notes in the radio frequency (rf) domain. The linewidth of the rf beatnotes is a direct measurement of linewidth of XUV comb teeth.

References

GENERATION AND PROPAGATION OF POLARIZATION
SINGULARITIES IN ISOTROPIC GYROTROPIC MEDIUM WITH
QUADRATIC AND CUBIC NONLINEARITY

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Earlier it was shown that in three-wave mixing processes and during self-action in isotropic gyrotropic medium
the radiation in signal beam is polarized inhomogeneously along the beam cross-section and may contain
polarization singularities. In our work we study their appearance in sum-frequency and second harmonic
generation at the surface and in the bulk of isotropic gyrotropic medium, and the interaction of polarization
singularities during self-focusing.

1. Introduction and formulation of the problem
Polarization singularities of the light field are points or lines in a cross section of a propagating beam, where the
intensity of one of the orthogonally polarized components of the beam becomes zero (generally they are called C-points
and L-lines). In this case either the orientation of the polarization ellipse or the polarization rotation direction becomes
indefinite. C-points can be classified as one of the following characteristic types known in literature: “star”, “lemon” or
“monstar” [1]. Polarization singularities are well known in linear optics, but there exist very limited number of works
on this subject involving nonlinear optics processes.

Earlier it was shown that in three-wave mixing processes [2-4] and during self-focusing [5] in isotropic gyrotropic
medium the radiation in signal beam is polarized inhomogeneously along the beam cross-section and this polarization
distribution may contain polarization singularities in certain cases. In our work we theoretically (analytically and
numerically) study the formation of these objects in three-wave mixing processes (sum-frequency generation – SFG,
and second harmonic generation - SHG) at the surface and in the bulk of isotropic gyrotropic medium, and the
interaction of polarization singularities during the self-focusing.

2. Discussion of results
We analyze and discuss the conditions of formation of singularities, their behavior on changing the parameters of the
initial beams and nonlinear medium, their morphology and characteristic features and connection with the symmetry of
the beam. In case of SFG by coaxially propagating beams in a bulk of the medium or by normally incident beams from
the surface of the medium, due to the symmetry of the problem, the signal beam also possesses a kind of symmetry
[2,3]. The appearance of the sum-frequency signal in these cases is forbidden within the framework of the plane-wave
approximation theory, however, accounting for the focusing of the incident beams and small longitudinal component of
the electric field in them, the appearance of the signal beam in this case can be explained. Under such conditions the
structure of the signal beam possesses a kind of symmetry, such, that the polarization state in the transversal section of
the beam depends only on the polar angle coordinate and does not depend on the distance from the center of the beam:
polarization remains the same along any straight line crossing the center of the beam. This symmetry makes impossible
observation any point singularities (like C-points) in perpendicularly reflected second harmonic beam. Instead of them
one can observe C-lines (lines of circular polarization – see fig. 1a) and L-lines, crossing the center of the beam (where
the intensity of light is zero). The conditions of the appearance of these singularities and analytical expressions for the
polar angles determining their position in the beam cross-section was found.

When proceeding to the oblique incidence from the normal incidence geometry, the symmetry of the problem and, thus,
of the reflected signal beam breaks. In this case there can appear C-points in the transversal section of the signal beam
(fig. 1b). Using the analytical formulae obtained in [4], we studied the conditions of appearance and the behaviour of
the C-points in reflected signal beam (in particular case of SHG), and also the way of the line-to-point singularity
transformation.

In self-focusing of the elliptically polarized beam in isotropic gyrotropic medium with spatial dispersion of cubic
nonlinearity, the polarization is varying along the cross-section of the propagating beam [5]. But in case of the radially
symmetric uniformly polarized Gaussian beam (without azimuthal angle dependence) at the entrance to the medium, the
propagating beam remains radially symmetric. In certain cases there can appear point of circular polarization in the
center of the beam, but it carries no topological charge since the azimuthal phase dependence is absent. Thus no C-point
appear in this case. However, if one considers inhomogeneously polarized beams at the entrance to the medium,
carrying the C-points, it will be possible to observe their nonlinear interaction.

We studied numerically interaction of the C-points in initial beams for different combination of their topological charge,
handedness and morphological type and we observed different scenarios of birth and annihilation of the C-points for all
these cases, comparing them with those in linear medium.
3. Conclusion.

In conclusion, we have analysed the formation, behaviour and the interaction of the polarization singularities (C-points) in three-wave mixing and in self-focusing processes in isotropic gyrotrropic medium with spatial dispersion of quadratic and cubic nonlinear optical response. We established the conditions of appearance of the C-lines and L-lines in symmetric sum-frequency and second harmonic beams obtained in case of SFG by coaxially propagating beams in a bulk of the medium or by normally incident beams from the surface of the medium. We have found the conditions of appearance of the C-points in SHG from the surface in case of oblique incident beam at fundamental frequency. We analysed in details the symmetry breaking of the beam and the transformation of polarization singularities when proceeding from the normal incidence geometry to the oblique one. We established that no C-points appear in the self-focusing of regular Gaussian beam, and we have studied numerically different scenarios of the interaction of the initial beams containing C-points for this case.

Figure 1: Polarization distribution in cross-section of second harmonic beam reflected from the surface of isotropic gyrotrropic medium in case of (a) normal and (b) oblique incidence of fundamental beam. Vertical C-line can be seen in (a) and C-point in (b) in the center of the beam is indicated by grey. The inset in the right upper corner in (b) shows the polarization streamlines (the main axes of the polarization ellipses are tangent to these lines in each point) in the vicinity of the C-point, and they represent “lemon” pattern.

References

NONLINEAR SPECTROSCOPY OF ONE-DIMENSIONALLY INHOMOGENEOUS MEDIUM WITH CUBIC NONLINEARITY

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The possibility of unique reconstruction of the spatial profile of the cubic nonlinear susceptibility tensor component of a one-dimensionally inhomogeneous plate whose medium has a symmetry plane perpendicular to its surface is proved and reconstruction algorithm is proposed.

1. Introduction

Control of the dielectric properties of one-dimensionally inhomogeneous structures is becoming a popular practical problem [1]. Different methods exist to solve this problem in linear media. However, most of these methods are either inapplicable in optics due to neglect of absorption [2] or frequency dispersion [3] or can be used only for weakly inhomogeneous media [1]. For nonlinear media, the solution of these problems is at the initial stage. In [4] we proposed a method for determining the coordinate dependences of the complex permittivity tensor components of a one-dimensionally inhomogeneous plate in linear media, the method being free from the above drawbacks. Now we generalize it to nonlinear media. As a result, we proposed the method of unique reconstruction of the coordinate dependence of complex cubic susceptibility tensor component \( \chi^{(3)}(z, \omega, -\omega, \omega, \omega) \) of a nonlinear medium whose dielectric properties change along the \( z \) axis that is perpendicular to its two parallel flat surfaces and arbitrary depend on the frequency.

2. Theory details

Let the layer of this medium adjoin the homogeneous isotropic linear media with a real dielectric constant \( \varepsilon_0 \) along the planes \( z = z_1 \) and \( z = z_2 \) \((z_1 > z_2)\). We assume that the medium producing the plate had a symmetry plane perpendicular to the surface. We will direct the axis \( x \perp z \) along this plane and assume that an \( x \)-polarized plane signal low-intensity wave propagating in the positive direction of the \( z \) axis is incident on this plate at a nonzero angle \( \alpha \). At \( z < z_1 \) the electric field strength of this wave is equal to \( E_0 \hat{e}_z \exp[i(\omega t - k_z z - k_x(z - z_1))] + c.\text{n.} \). Here, \( \hat{e}_z \) is the unit vector perpendicular to the symmetry plane of the medium; \( k_x = k_0 \sin \alpha; k_z = k_0 \cos \alpha; k_0 = \omega_0 \sqrt{\varepsilon_0 / c}; c \) is the speed of light in vacuum. In addition, let an intense fundamental-radiation plane wave with the electric field strength equal to \( E_0 \hat{e}_z \exp[i(\omega t - k_0(z - z_1))] + c.\text{n.} \) at \( z < z_1 \) be incident on a plate perpendicular to its surface.

We assume that as the phase-matching condition is violated, harmonics are not generated in the plate. As a result, only three waves [one intense \( (E_0 \hat{e}_z \exp[i(\omega t) + c.\text{n.}] \) wave and two weak waves: the initial signal wave and a new \( (E_0 \hat{e}_z \exp[i(\omega t + k_x z)] + c.\text{n.}) \) wave produced in the nonlinear medium] with the frequency \( \omega_0 \) can efficiently interact. Because the medium is inhomogeneous, each of these waves is a superposition of two counter-propagating variable-amplitude travelling waves. To describe their propagation, we can use both a system of six exact first-order equations for travelling-wave amplitudes and a system of three second-order wave equations for the total electric field of each wave. For the problem under study, using the second-order equations is more preferable, because it allows one to simplify the presentation.

The new wave \( E_0 \hat{e}_z \exp[i(\omega t + k_x z)] + c.\text{n.} \) appears during the nonlinear interaction of intense and signal waves and, in turn, can affect propagation of the latter. This nonlinear interaction takes place because the plate medium has a nonlinearity that is characterized by a cubic susceptibility tensor \( \chi^{(3)}(z, \omega, -\omega, \omega, \omega) \). Because the medium has a plane of symmetry \( m_x \), we can write the following equations for waves propagation:

\[
\frac{d^2 E_0}{dz^2} + 0.5 \omega^2 \varepsilon_0(z) E_0 / c^2 = 0. \tag{1}
\]

\[
\frac{d^2 E_0}{dz^2} + \left[ \omega^2 \varepsilon_x(z) / c^2 - \lambda \right] E_0 + r(z) E_0^* = 0, \quad \frac{d^3 E_x}{dz^3} + \left[ \omega^2 \varepsilon_x(z) / c^2 - \lambda \right] E_x^2 + r^* E_x^* = 0. \tag{2}
\]

where \( \lambda = k_x^2, \varepsilon_x(z) = \varepsilon_y(z) + 8\pi \chi^{(3)}(z) E_0^2 / c^2 \), and \( r(z) = 4\pi \omega \chi^{(3)}(z) E_0^2 / c^2 \).

Because of Maxwell’s boundary conditions on the layer surface, we have

\[
E_0(z_1) = (1 + R) E_0, \quad \frac{d E_0}{dz} \bigg|_{z=z_2} = -i k_0 E_0, \quad \frac{d E_x}{dz} \bigg|_{z=z_2} = i k_0 E_x(z_2) = 0. \tag{3}
\]

\[
E_0(z_1) = (1 + R) E_0, \quad \frac{d E_0}{dz} \bigg|_{z=z_2} = -i k_0 (1 - R) E_0, \quad E_x(z_1) = TE, \quad \frac{d E_x}{dz} \bigg|_{z=z_2} = -i k_0 TE. \tag{4}
\]
Here, $R$ is the amplitude complex reflectivity of signal wave by the plate and $T$ is the amplitude complex transmittivity of this wave through the plate. The new wave $E_0(z)$ appearing in the plate during the nonlinear interaction propagates in homogeneous linear media adjacent to nonlinear medium in the form of a wave $E_{g1}(z) \exp[i(\omega t + k_g x + k_g (z - z_j))] + \text{c.c.}$ at $z < z_j$ and in the form $E_{g2}(z) \exp[i(\omega t + k_g x - k_g (z - z_j))] + \text{c.c.}$ at $z > z_j$. In this case, $E_0$, $E_{g1}$ and $E_{g2}$ meet Maxwell’s boundary conditions

$$E_{g1}(z_j) = E_{g1}, \quad \frac{dE_{g1}}{dz} \big|_{z=z_j} = i k_g E_{g1}, \quad E_{g2}(z_j) = E_{g2}, \quad \frac{dE_{g2}}{dz} \big|_{z=z_j} = -i k_g E_{g2}. \quad (5)$$

It follows from equations (2), (4), and (5) that $E_{g1}$ and $E_{g2}$ are proportional to $E$ for these $\varepsilon_{\chi}(z)$ and $r(z)$. It means that we can introduce $E$-independent signal-wave conversion coefficients $G^{(1)} = E_{g1}/E$ and $G^{(2)} = E_{g2}/E$ characterizing the conversion efficiency of the signal wave incident on the plate into the waves of the same frequency, propagating away from the plate. In this case, the propagation direction of the latter ones differs from the propagation direction of reflected and transmitted signal waves. Using these coefficients, boundary conditions (5) can be conveniently rewritten in the form

$$E_{g1}^{(\chi)}(z_j) = G^{(1)} E, \quad \frac{dE_{g1}}{dz} \big|_{z=z_j} = -i k_g G^{(1)} E, E_{g2}^{(\chi)}(z_j) = G^{(2)} E, \quad \frac{dE_{g2}}{dz} \big|_{z=z_j} = i k_g G^{(2)} E. \quad (6)$$

3. Results and discussions

If the dependences $\varepsilon_{\chi}(z)$ and $r(z)$ are known, having solved equations (2), (4), and (6), we can unambiguously calculate $R$, $T$, $G^{(1)}$, $G^{(2)}$ for any angles of incidence of a plane signal wave. We proved that the converse is also true: if in some interval of angles of the plane signal wave incidence we have measured the amplitude complex transmission, reflection, and conversion coefficients in the presence of an intense fundamental-radiation wave, the dependences $\varepsilon_{\chi}(z)$ and $r(z)$ for a layer of the given thickness can be unambiguously found with the help of the obtained data. The linear dielectric constant profile $\varepsilon_{\chi}(z)$ can be also uniquely reconstructed, as follows from papers [4, 5], by the amplitude reflectivities and transmittivities of the signal wave in the absence of an intense fundamental-radiation wave. If the dependences $\varepsilon_{\chi}(z)$, $r(z)$, and $\varepsilon_{yy}(z)$ are found, $\chi_{yyyy}(z, \omega; \omega, \omega, \omega)$ can be uniquely reconstructed with the help of one of two equivalent expressions:

$$\chi_{yyyy}^{(3)}(z, \omega; \omega, \omega, \omega) = [\varepsilon_{\chi}(z) - \varepsilon_{yy}(z)]/(8\pi |E_f(z)|^2) = c^2 r(z)/(4\pi \omega^2 E_f^2(z)), \quad (7)$$

which follow from the definitions of the quantities $\varepsilon_{\chi}(z)$ and $r(z)$ presented after the system of equations (2). The strength $E_f(z)$ entering into (7) is unambiguously found from equation (1), (3).

Thus, we have obtained the following result. Let the profile of the linear dielectric constant of the plate $\varepsilon_{yy}(z)$, be known and, the amplitude complex reflection $R$, transmission $T$, and conversion coefficients $G^{(1)}$, $G^{(2)}$ of the signal wave in some interval of angles of the plane signal wave incidence be measured in the presence of the intense fundamental-radiation wave with the known amplitude $E_f$. These data will be sufficient to find unambiguously the cubic nonlinear susceptibility $\chi_{yyyy}^{(3)}(z, \omega; \omega, \omega, \omega, \omega)$ of the plate under consideration. Due to the proven uniqueness of the reconstruction, its finding can be reduced to searching for a unique zero minimum of a specific functional, for example, analogous to that proposed in [4, 5].

References

Due to high special resolution and interference nature, CARS is well suited for the diagnostics of transparent nanocomposite systems and, in particular, is very efficient for diagnostics of fluid phase behavior under nanoconfinement. Adsorption of a gaseous fluid on the walls of nanopores and condensation in their volume leads to obvious transformation of the molecular spectra. Recently we have developed a model which describes the behavior of molecular spectra at isothermal compression in cylindrical nanopores. Calculations based on the model have shown a good agreement with the experimental results for carbon dioxide in nanoporous glass with pores of diameter of several nanometers. Here we use the developed approach to investigate the phase behavior of carbon dioxide in glass nanopores at near-critical temperatures. It has been experimentally shown that condensation in nanopores occurs at relatively low pressures at subcritical and even at supercritical temperatures. The analysis based on the developed model allows to reveal some qualitative and quantitative characterizations of the shift of critical point.

In a large number of applications of the nanocomposites, the fluid component is a chemical reagent or a transport medium. The chemical and physical properties of the fluid play the key role in such functional systems, and these properties are naturally determined by the phase state of the fluid. The fluid phase behavior substantially depends on the pore sizes, their interconnection, and other topological and morphological peculiarities. Transparent nanoporous materials provide a good opportunity for observation of molecular media under nanoconfinement by means of optical methods. Available transparent materials like nanoporous glasses, polymers, aerogels, zeolites with a wide range of pore radii and morphology allow to realize different confinement geometries.

In view of high spacial resolution, CARS is well suited for probing the internal areas of 3D nanoporous host [1]. CARS spectroscopy allows diagnostics of a fluid phase behavior by the direct probe of its molecular vibrations. Indeed, each phase (gaseous, adsorbed, or liquid-like) of a fluid is characterized by its specific vibrational spectrum; therefore the phase composition in the system can be determined by analysis of the inhomogeneous lineshape. CARS has proved its efficiency for diagnostics of the phase behavior of carbon dioxide in glass nanopores with diameter of several nanometers [2]. Thermodynamic concept of adsorption and condensation in cylindrical nanopores was used to calculate the corresponding spectral shapes [3]. The results of calculations appeared to be in a good agreement with CARS spectrum transformations obtained in experiment [4]. The interference nature of CARS provides simultaneous probing of both the fluid and the porous host and, therefore, allows to characterize both the fluid phase composition and the host porous structure [4].

Here we expand the developed approach to the diagnostics of fluid phase behavior in nanopores near the critical temperature. The transformation of carbon dioxide spectra obviously shows the condensation inside the glass nanopores at relatively low pressures at subcritical and even at supercritical temperatures. The analysis based on thermodynamics allows to reveal some qualitative and quantitative characterizations of the shift of critical point.

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References
In laser ultrasonics the lasers are applied for generation and detection of the acoustic waves at frequencies below 1 GHz, while in picosecond laser ultrasonics the femtosecond lasers are used for all-optical monitoring of the acoustic waves in the GHz-THz frequency range. The first decade of the 21st century is marked by an important progress both in laser ultrasonics and in picosecond laser ultrasonics (hypersonics). The number of possible applications of these techniques is continuously growing.

1. Achievements

Laser ultrasonics has been recently successfully applied in resonance ultrasonic spectroscopy and in nonlinear acoustic imaging of the cracks. Picosecond laser ultrasonics has been successfully applied for the generation and detection of the acoustic solitons and plane shear acoustic waves, evaluation of supersonic expansion of the photo-generated electron-hole plasma in semiconductors, diagnostics of the physical properties of solid/solid and solid/liquid interfaces and non-destructive testing of nanomaterials and nanostructures, including depth-profiling of the elasticity of submicron thick films with a spatial resolution of a few tens of nanometers. Both laser ultrasonics and picosecond laser ultrasonics has been applied for the evaluation of material properties at high pressures in diamond anvil cells. Important progress has been achieved in the development of optically-controlled piezoelectric emitting transducers operating in GHz-THz frequency range, which are more efficient than the optoacoustic transducers based on thermoelectric or electron-hole-phonon deformation potential effects.

2. Perspectives

The perspectives for the nearest future are related to extending the applications of laser-generated acoustic waves (in particular, inhomogeneous plane bulk acoustic waves) to the evaluation of nanomaterials, nanostructures, biological objects at micro and nano scales, and also to the investigation of ultra-fast acoustic phenomena in liquids and glasses. The progress is expected through the development of the advanced methods of the hypersound generation, for example with the use of nanomaterials, such as graphene, and the nanostructures, as well as through the application to hypersound detection of ultrafast optical interferometry and polarimetry in additional to traditional reflectometry. It is also expected that the development of the picosecond acoustic microscopy with nanoscale lateral and in-depth spatial resolution will be reported in the nearest 1-2 years.
LASER PROCESSING OF CFRP

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The key issue for laser-processing of carbon fiber reinforced plastics (CFRP) is the thermal damage of both, the matrix material and the carbon fibres. This paper describes the basic mechanisms leading to such thermal damage and its implications on the design of appropriate laser processing systems.

1. Introduction

The mass production of light-weight constructions with carbon fibre reinforced plastics (CFRP) requires large-series capable processing methods. Laser processing is a widely accepted and industrially approved materials processing technology, especially for automotive components. Unfortunately, CFRP exhibits very inhomogeneous optical and thermal properties together with a very low thermal damage threshold of the plastic matrix. Therefore the laser processes which are well established for metals cannot easily be transferred to CFRP laser processing. The main issue are the often reported large thermally damaged regions [1][2][3]. However, it is also possible to process CFRP with a high quality as reported in [4][5] and shown in Figure 1 (left), but only with average process speeds which are not suited to industrial needs.

This paper gives an overview over the state of the art in laser processing of CFRP. The fundamental limitations caused by heat conduction and heat accumulation will be discussed and corresponding basic experiments will be shown giving an insight into the mechanisms of laser CFRP-processing. The findings help to define the suitable parameters for laser processing of CFRP with high quality and high productivity will be used as constraints for the corresponding system design.

2. Thermal damage

Basic thermal conductivity calculations under the idealized condition of a top-hat beam profile and for cw and single-pulse processing show [1][6] that a minimum thermal damage cannot be avoided as shown in Figure 1(right) but that its extent is strongly depending on the laser intensity. The red line is the extent of the matrix evaporation temperature, the blue dashed line the extent of the matrix structure damage temperature as a function of the absorbed intensity. Published experimental values shown as data points in Figure 1 (right) confirm this finding. However, if an intensity of about 10⁹ W/cm² is exceeded, the damage appears no longer to be dominated by the single pulse behaviour as assumed in the model. At high intensities, short-pulse laser systems with high repetition rates in fundamental mode are used. Therefore, heat accumulation and beam profile effects have to be considered. In addition, plasma absorption and scattering begins to play a role.

In most applications the extent of the material damage should be kept well below 100 µm. Considering the additional damage effects encountered in the experiments, the intensity range of “optimum processing” is between 10⁸ W/cm² and 10¹² W/cm² shown as shaded area in Figure 1 (right).

3. Basic experiments

High-speed records of the CFRP-surface were taken in order to investigate the development of the thermally damaged zone. Figure 2 (left, right) shows single frames out of a 3000 fps record. Figure 2 (left) shows a CFRP-cut made with 22 W of average laser power, 8 ps pulse duration, a focus diameter of 30 µm, at a repetition rate of 800 kHz and a wavelength of 515 nm. The feed rate was set to 2 m/min. A relatively large region of evaporated matrix material of about 200 µm is produced. The maximum extent is reached 100 µm in the lag of the processing laser corresponding to a delay of about 3 Milliseconds confirming the slow propagation of the heat wave along the carbon fibres. In Figure 2...
the laser pulse division was set to select every tenth pulse. With it, the average power is reduced to 2.2 W and the frequency to 80 kHz. In addition the feed rate was increased to 10 m/min. With this setup the heat accumulation is almost completely avoided clearly proving its influence as all other parameters were kept constant. A calculation of the heat accumulation for the corresponding laser parameters (assigned with the black arrows) is shown in Figure 2 (middle). It clearly demonstrates the difference in temperature increase for the two parameters.

![Figure 2. High-speed records of the growth of the thermal damage at 800 kHz, 22 W, 2 m/min (left), calculated heat accumulation (middle), and 80 Hz, 2 W, 10 m/min (right) ](image)

### 4. Implication on system design

The knowledge of these fundamental thermal limitations is very useful as they directly impact the layout of appropriate processing systems [9]. Industrial mass production, such as for example laser cutting and welding in automotive industries, demands average processing speeds in the range of 10 m/min. This value has to be reached as well with CFRP material which typically has a thickness of 2 mm for such applications. Therefore a laser source with an average power of ≈5 kW is required, taking 60 J/mm³ of process energy, a kerf width of 200 µm (convenient aspect ratio ≈10) and an absorptivity of 80%. Together with the above mentioned limiting values, estimates for system performances with cw and pulsed lasers can be given:

With a 5 kW cw laser, the intensity of 10⁸ W/cm² requires focussing to a focus diameter of about 80 µm. Taking the aspect ratio of ten and with it the 200 µm kerf width into account, this requires a multipass processing strategy with about 15 passes yielding a single pass (“effective”) feed rate of 150 m/min. The focus position tolerance is about 150 µm (half a Rayleigh length) and the lateral position accuracy <10 µm. This has to be achieved in 3D-contour lengths of a few meters. High-quality processing at 10⁹ W/cm² with minimum damage below 10 µm would increase the requirements regarding effective processing and positioning accuracy one order of magnitude.

Picosecond pulsed lasers have a very high peak power. Therefore the focal spot should be as large as possible, i.e. of the same size as the kerf. Limiting the intensity to 10¹² W/cm² to reduce plasma effects clearly defines the laser source which must be run at 1.6 MHz at a pulse energy of about 3 mJ. Allowing a pulse-to-pulse overlap of 90% (which might already be critical regarding heat accumulation) a feed rate of about 2000 m/min is necessary and with it about 200 passes.

Values in between the parameters for picosecond and the cw processing are obtained with nanosecond laser systems.

### 5. Summary

In summary it was shown that basic physical effects create strong boundary conditions for CFRP laser processing. The knowledge of these conditions is very useful to achieve appropriate process quality. However, these limitations directly impact the system design. To achieve similar average processing speeds as with today’s industrial sheet metal processing machines very high performance is required which is not yet available. Therefore the realisation of such “next generation” processing systems is a very challenging task.

### 6. References

Various regimes of surface and bulk micro and nanostructuring of diamond determined by its laser-induced transformation into graphitic phase will be presented. It will be also shown that laser application can result in local area CVD diamond growth. CVD reactors for large area diamond deposition based on laser-produced stationary plasma in a gas stream have been also proposed and developed.

It will be shown that intensive laser radiation is a perfect tool for processing of diamond materials: single crystal, poly and nanocrystalline diamond, amorphous diamond-like coatings, micro and nanoparticles. Methods of synthesis and major properties of these materials, such as optical absorption and thermal conductivity, will be briefly reviewed.

Emphasis on the mechanisms and general futures of laser induced surface and bulk graphitization of diamond will be made. Two basic regimes of diamond ablation (vaporization and oxidation of the laser graphitized diamond surface) will be considered. The specific feature of short-pulsed laser ablation – possibility to remove ultra-thin layers of the diamond material as a result of combined physical and chemical surface treatment (nanoablation) will be discussed.

Basic processing operations will be presented. They include diamond polishing and shaping, production of conductive pathways, micro and nanostructures on the diamond surface, such as diffractive optical elements. The possibility to laser produce conductive and hollow structures in the diamond bulk, including curved features, will be demonstrated.

The techniques of laser assisted diamond CVD, that allow to produce smooth or selective area grown films will be presented. Large area chemical vapor deposition of diamond by means of CO\(_2\)-laser plasmatrons in Ar:H\(_2\):CH\(_4\) gas streams and diamond-like coatings deposition via laser ablation of graphite in vacuum will be also discussed.

The summary of the presented data can be found in [1].

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References
LASER-BASED METHODS FOR MICROVASCULAR IMAGING IN HUMANS

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Abstract:

Our health has been transformed by advances in physics. This trend continues and means there is an explosion of interest in developing and evaluating new tools to study the microcirculation. Perhaps more than this, it heralds the arrival of 3D and 4D imaging. Biophotonics promises 3D microcirculation imaging at clinically relevant speeds and depths. Photonics promises to bring healthcare to the next level, as it is the only means to see cells and molecules in small, accessible, low cost and safe imaging systems. Recently high resolution label-free imaging of the microcirculation at clinically relevant depths and has become available in research labs. The number of papers on the microcirculation published in physical sciences doubled between 2006 and 2008 representing a jump from the long stable 5% of all microcirculation papers to 20%. This paper will present the current status of microcirculation imaging and some results from our own work.

1. Introduction

The microcirculation is a key component of several body functions including regulation of blood pressure, flow and body temperature, delivery of nutrients and removal of metabolic waste products. Living longer has exacerbated the challenges of diabetes and cancer, which have their origins and clinical manifestation in the microcirculation. Physics has delivered X-Ray, CT, MRI, ultrasound, PET and radiotherapy. Our health has been transformed by these advances. Photonics promises to bring healthcare to the next level, as it is the only means to see cells and molecules in small, accessible, low cost and safe imaging systems. The number of papers on the microcirculation published in physical sciences doubled between 2006 and 2008 representing a jump from the long stable 5% of all microcirculation papers to 15% (Fig. 1). Recently high resolution label-free in vivo tomographic imaging of the microcirculation at clinically relevant depths and has become available in research labs [1] and some tomographic systems are now commercially available for pre-clinical use on small animals. Uptake in the clinic requires the ability to address a need and important physiological events often happen over periods of seconds; heartbeat, breathing, endothelial dependent and other forms of vasomotion. We have developed 1D (laser Doppler), 2D (TiVi), 3D and 4D (cmOCT) [2] systems for imaging the microcirculation [1-7]. These new imaging systems based e.g. on optical coherence tomography and photoacoustic microscopy take some hours to process 3D images of the microcirculation and often the images require significant ‘touch-up’. Several groups are pushing these technologies to clinically relevant speeds and depths.

Figure 1: Graph depicting the increase in the number of publications using the search term ‘microcirculation’ (Source: Scopus). Blue squares: all publications; pink squares: physical sciences; yellow triangles: based on the laser Doppler modality.
2. Methods and Results
We employed a Thorlabs (OCM13000SS) swept source OCT system with a lateral resolution of 25 µm and used a dense scanning method as per the cmOCT methodology described previously [2] to scan an area of 500 µm x 500 µm on the volar forearm of a young adult volunteer. After 20 s registering the resting flow, the brachial artery was occluded for 20 s. The OCT data was recorded for a further 55 s and a typical result after cmOCT processing is shown in Fig. 2.

![Figure 2](image.png)

Figure 2: Graph depicting the response of a single capillary in the volar after occlusion of the brachial artery in a young adult volunteer.

3. Conclusions
Since each white pixel indicates moving blood, the volume fraction of tissue with moving blood was shown to increase rapidly after release of occlusion. This is the expected reactive hyperaemia and several other examples including reactive hyperaemia at several depth will be shown.

References
We analyze the peculiarities of far-field diffraction patterns resulting from the scattering of a laser beam by an ensemble of non-overlapping elliptical discs modeling red blood cells (RBC) elongated by shear stress in ektacytometer. In the case of a variance in the disc shapes modeling the variance in shear-induced deformation of RBC, the isointensity lines of the diffraction patterns become non-elliptical. We propose an algorithm allowing for the estimation of RBC deformability distributions in the population. The analytically derived estimates fit well the experimental results obtained by numerical processing the diffraction patterns measured in the particular case of bimodal distributions of RBC deformability.

1. Introduction and motivation

Ektacytometry is a conventional technique widely used for the *in vitro* analysis of the ability of RBC to reversibly change their shapes under shear stress. The technique is based on processing the diffraction patterns obtained in the far field zone at different shear stresses under laser illumination of a highly diluted suspension of RBC moving in a thin rheological gap of a Couette cell. Conventionally, ektacytometer measures only one parameter, the so-called deformability index, averaged over many thousand cells illuminated by the laser beam during the signal sampling. However, different particles in a population of live cells have different abilities to deform. In this regard, conventional deformability can be regarded as a statistical characteristic of an ensemble of particles that can be used for defining the distribution function, mean value and variance. In this work, we consider a problem of how the difference in particle shapes affect the shape of the diffraction pattern detected in laser diffractometry of erythrocytes. The aim of the work is to analytically find the relation between the characteristics of the diffraction pattern and the variance in the shape parameter of the particles.

2. Theoretical consideration

According to our analysis, the diffraction pattern resulting from the scattering of a laser beam by an inhomogeneous ensemble of RBC should have characteristic peculiarities. In order to make the analytical analysis feasible we approximate the erythrocyte by a transparent elliptical disc. This assumption is based on the images of erythrocytes in shear flows obtained with a microscope [1]. We assume the semi-axes of an elliptical disc *a*, *b* to be random values:

\[a = a_0 \cdot (1 + \varepsilon), \quad b = b_0 \cdot (1 - \varepsilon)\]

Here *a_0*, *b_0* - mean values of the semi-axes, \(\varepsilon\) - random shape parameter of the particle. We assume that \(\langle \varepsilon \rangle = 0\) and \(\langle \varepsilon^2 \rangle \equiv \mu^2 \ll 1\). Using the approach developed on the basis of anomalous diffraction approximation in [2,3], we obtained the following approximate analytical equation for the distribution of the light intensity on the observation screen in the vicinity of the central maximum of the diffraction pattern:

\[f = \frac{1}{4\beta^2} \cdot \frac{I}{I(0)} = (1 - r^2) + \mu^2 \cdot \cos^2 2\varphi.\]  

(1)

Here *r* - scattered light intensity, *I(0)* - intensity of the central maximum of the diffraction pattern. The polar coordinates \(r, \varphi\) are defined as: \(x/A = r \cdot \cos \varphi, \quad y/B = r \cdot \sin \varphi\), where \(x, y\) - Cartesian coordinates of the measurement point of the observation screen, *A, B* - parameters determining the size of the diffraction pattern: \(A = q_1z/(k a_0), \quad B = q_2z/(k b_0)\). In these formulas \(z\) - distance from the measurement volume to the observation screen, \(k = 2\pi/\lambda\) - wave number, \(\lambda\) - wavelength. The constant values \(q_1 = 3.82\) and \(\beta = -0.4\) are the parameters of Bessel function.

Basing on the equation (1) we have designed several methods of evaluation of the parameter \(\mu\) making use of the laser diffractometry data. One of them is described by equations

\[\mu = \sqrt{f - [1 - P \cdot (1 - \sqrt{f})]^2}, \quad P = \sqrt{x_0^2 + y_0^2}/(l\sqrt{2}),\]  

(2)

where the values \(x_0, y_0\) and \(l\) are parameters of an isointensity curve, shown in Fig. 1.3.
Thus we show a principal possibility of measuring such characteristics of RBC ensemble as particle shape parameter variance by means of laser diffractometry.

3. Experimental verification

In order to verify our analytical results in a particular case of bimodal distribution of cells shapes, we have performed diffractometry tests with normal rat RBC and those rigidified with glutaraldehyde following the earlier experiment described in [4]. Figure 1.1 shows the diffraction pattern obtained from a suspension of freshly drawn rat RBC showing normal deformation under shear stress equal to 44 Pa. In this case the isointensity curve semi-axes ratio $a/b \approx 3$. Figure 1.2 shows a pattern obtained in similar conditions from a 1:1 mixture of the suspension of freshly drawn rat RBC and those rigidified with glutaraldehyde. This mixture mimics the bimodal distribution cells shapes at a fixed shear stress. Figure 1.3 shows the isointensity line obtained by processing the diffraction pattern shown in Fig. 1.2, and corresponding to $f = 0.15$.

![Diffraction patterns](image)

Figure 1: Experimental diffraction patterns from ensembles of RBC with: 1 – homogeneous and 2 – bimodal distributions of shear induced elongation; 3 – isointensity line derived from the experimental diffraction pattern related to ensemble of RBC with a bimodal distribution of their shear induced elongation.

In this case, using equations (2) and data received from Fig. 1.3 we have calculated experimental value $\mu = 0.29 \pm 0.03$. On the other hand, the bimodal ensemble of cells under investigation can described as follows: $a_1 = a_0 \cdot (1 - \mu)$, $b_1 = b_0 \cdot (1 + \mu)$, $a_1 = b_1$ for rigidified cells, and $a_2 = a_0 \cdot (1 + \mu)$, $b_2 = b_0 \cdot (1 - \mu)$, $a_2 = 3b_2$ for normal cells under given shear stress. Consequently, we obtain the theoretical value $\mu = 2 - \sqrt{3} \approx 0.29$. Close coincidence of the results proves the adequacy of the applied approach.

4. Conclusion

In addition to conventional operation, the Couette type laser diffractometer can, in principle, be used for measuring light intensity distributions in the diffraction patterns with isointensity curves other than elliptical thus yielding additional information on subpopulations of RBC with different shear-induced deformations. Practical implementation of the proposed new possibilities will allow for significantly broadening the functionality of laser ektacytometry as a technique for complex in vitro diagnostics of RBC.

References


LASER-INDUCED NANOPARTICLE DELIVERY AND IMPACT ON CELLS AND TISSUES

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Diagnostic and therapeutic technologies rely on nanoparticle delivery into a tissue and their usage as contrasting agents or mediators of cell laser heating will be presented. Delivery of titanium dioxide, zinc oxide, and gold nanoparticles which are often used as contrasting agents for optical coherence tomography (OCT) and serve as carriers for drugs and other formulations will be discussed. Several other laser-based technologies such as gold nanoparticle photothermal treatment of tumors, killing of microorganisms using photocatalytic TiO₂ nanoparticles, gold nanoparticles and their conjugates with the photodynamic dyes will be analyzed. As one of the novel technologies for drug and nanoparticle delivery, erbium laser fractional microablation (ELFMA) will be presented.

On the cellular level a novel thermal effect – hoop-shaped hot zone on the nanoshell surface, can be used for precise laser-induced optoporation and nanosurgery of cells [3, 4].

OCT can be an effective method for monitoring of nanoparticle delivery into skin [1]. The method is based on the high refractive index mismatching between biological tissue components and metal nanoparticles that causes the high contrast imaging. The typical depth of nanoparticle delivery and OCT probing at ELFMA is about 500 µm. For example, a papillary structure on the epidermis/dermis junction became clearly visible. After the restoration of the skin integrity, the nanoparticles, inserted at the depth exceeding the epidermis thickness (100–150 µm), stay in the dermis, providing amplified skin scattering.

Nanoparticle application is also of great interest for the reduction of the tooth sensitivity, restoration and strengthening of enamel, and cosmetic whitening. Using OCT, the penetration of TiO₂ nanoparticles (size < 100 nm) from a suspension in Poly(sodium4-styrene-sulfonate) with the concentration of 10 mg/mL into the tooth dentin and enamel samples was studied [1]. The A-scan slope changes with incubation time, and the greatest increase of the signal (up to 5 dB) was observed directly under the surface and at the depths of 300–600 µm from the surface of the sample.

The basic principles, recent results, advantages and limitations of laser-induced nanoparticle delivery in application to cell biology and medicine will be discussed.

Several promising diagnostic and therapeutic technologies rely on nanoparticle delivery into a tissue and their usage as contrasting agents or mediators of cell laser heating [1-4]. An important problem is the nanoparticle delivery and distribution in the tissues and organs. Titanium dioxide, zinc oxide, and gold nanoparticles are often used as contrasting agents for optical coherence tomography (OCT) of skin [1]. Nanoparticles also serve as carriers for drug and other therapeutic and diagnostic formulations delivery. Gold nanoparticles are often used for photothermal treatment of tumors [5]. Photocatalytic properties of TiO₂ nanoparticles [6], as well as gold nanoparticle laser-induced heating alone and in combination with photodynamic dyes [7] provide phototoxic action on pathogenic microorganisms. The main advantage of transcutaneous administration of the formulations (including nanoparticles) is that the delivery is targeted directly to the pathologically modified areas of the tissue [1, 2]. Erbium laser fractional microablation (ELFMA) of tissues is one of the promising technologies for nanoparticle transcutaneous delivery [2].

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References
Nanodiamond is considered as a promising nanomaterial for bio applications due to its bio-compatibility and physical-chemical properties including spectroscopic properties, photoluminescence and Raman. In bio-labeling or imaging, conjugated bio-molecules serve for specific or non-specific interaction with target whereas ND spectroscopic signal are used for detection. For the successful development of nanoparticles bioapplications, the mechanisms and character of interaction with living organism are important subjects of study. The interaction of various kinds of nanodiamonds with living systems, like cells, tissues, microorganisms etc., are discussed from points of view both bioapplications and nanosafety.

Diamond nanoparticles (nanodiamond, ND) are considered promising for biological applications such as imaging and biolabeling, drug delivery, biomolecule target capturing, biosensors, etc. [1-6], due to its physical-chemical properties, structure, high chemical stability and biocompatibility. ND’s surface can be easily functionalized with various molecular and ionic groups and then connected with biomolecules of interest via physical adsorption or chemical linking. Spectroscopic properties of NDs make them convenient for development of bio-labels. For bio-labeling or imaging, attached (conjugated) molecules serve for specific or non-specific interaction with target; whereas ND spectroscopic signal (Raman and luminescence) are used for detection. Photoluminescence (PL) of NDs is determined by concentration and nature of the crystal lattice defects (particularly, NV centers) as well as by nanosize effect. The use of Raman signal of NDs for bio imaging taking advantage of high spectral and spatial resolution [1-4]. Raman signal of ND (phonon mode of sp3-bonded carbon) is strong and isolated, can be excited by wavelength in a wide interval, no photobleaching take place, etc. [5].

For the successful development of nanoparticles bioapplications, the mechanisms and character of interaction with living organism are important subjects for study. The ND interaction with various cell cultures in-vitro has been studied and ND biocompatibility and non-cytotoxicity have been demonstrated in wide range of ND concentrations. It can easily penetrate into the cells and accumulate inside. For specific interaction with cellular elements, e.g. for biolabeling, as well as for drug delivery, different methods of functionalizing the ND surface and conjugation are recently developed, together with the methods of targeted delivery and drug release [2, 6, 7]. The information about ND interactions with living organisms as well as with organs and tissues is more limited. Concerning the tissues, the studies of ND effect on blood and skin can be mentioned [8, 9]. The examples of ND interaction with whole organisms by in vivo tracking the fluorescent ND in nematode C. elegans has been demonstrated [10], as well as entrapping of ND injected in the blood system of mouse (in liver) has also been observed [11].

Together with nanoparticles bioapplications, the development of nanotechnologies raises questions of safety of nanomaterials used; including nanosafety in technological process and the estimation of environmental risks. Accordingly, the investigation of effects on various kinds of protists microorganisms is important. The protists unicellular microorganisms ciliated protozoa are the key members of many ecosystems. These microorganisms are widely used as model system for study the toxicity of environmental agents; and on the other hand, ciliated protozoa are very well studied and extensively used as a model organism in cell biology, genetics studies, etc. Protozoa can feed on suspended particles in range of sizes from nm to microns. To study the biodistribution of the internalized nanoparticles and of their toxic effects and to develop the methods of in vivo imaging of the whole organism, these are convenient system for investigation. However, only limited studies concern protozoa microorganisms used for the evaluation of biological effects of engineered nanoparticles, particularly the observation of fluorescent QD inside the ciliate protozoa was reported [12, 13]. We study the interaction of ciliated eukaryotic unicellular organisms Paramecium caudatum and Tetrahymena thermophiles with different kinds of NDs. The protozoa growth and functioning in the presence of various kinds of ND are analyzed. The engulfment and trafficking of NDs of sizes 5 and 100 nm in the microorganisms were investigated. The entering ND into the microorganisms together with the bacteria (E. coli, after interaction with 5 nm ND) and ND distribution inside also was studied. The 100 nm ND was demonstrated to be non-toxic for the protozoa organisms and its luminescence properties make it convenient for the imaging and trafficking of matter delivery. As an example, in the Fig. 1 the ND localization in food vacuoles of P. caudatum is shown. The ND luminescence is excited with 488 nm wavelength and the signal is collected in range 500-530 nm. Corresponding PL spectrum of 100 nm ND is presented in the Fig. 2.
Figure 1  Set of microscopic images of *P. caudatum* at scan along Z axis obtained using the Leica confocal laser-scanning microscope (TCS SP5, Germany) equipped with an argon laser (457/488/514 nm). *P. caudatum* was grown in straw medium and feed on 100 nm ND. To observe food vacuoles LysoTracker Red DND-99 (Sigma) was used (Excited by using 543 nm laser and collected in 555 to 600 nm, marked in red; the ND luminescence is excited with 488 nm wavelength and the signal is collected in range 500-530 nm (marked in green). The localization of ND predominantly coincides with vacuoles

Figure 2  Luminescence spectrum of 100 nm ND at excitation 488 nm (measured with a-SNOM Witec, Germany)

In conclusion, in this work, in addition to previous studies of ND interaction with cells and ND use for imaging and materials (drugs, gns, etc.) delivery in *in-vitro* cultured cells and first, very few investigations of effects on tissues and animal organisms, the ND interaction with unicellular microorganisms is observed; using this model system for understanding the mechanisms of interaction, for in-vivo observations, and development of ND bio-applications is discussed.

References

In this work we present a detailed study of the Raman spectra of random copolymers of ethylene and propylene with a number of \( \alpha \)-olefins, and investigate the relationships between the spectral characteristics of the Raman lines and the copolymer structural properties.

Polyethylene (PE) and isotactic polypropylene (PP) are important industrial polymers with interesting physical and chemical qualities. However, their properties can be further improved or tuned by the induction of chain branching through copolymerization with \( \alpha \)-olefins. Random copolymers are the most promising industrial fabrics, as they exhibit an abrupt decrease in the degree of crystallinity with the increase in the incorporated monomer content. This allows tuning the copolymer mechanical characteristics from rigid to elastic as a function of the incorporated monomer content. Moreover, the copolymers are of significant interest for both industrial and scientific research, since their vibrational spectra, their molecular and supramolecular structure, and their deformation mechanisms demonstrate new interesting features compared to the homopolymers.

Raman spectroscopy is a highly informative technique for the study of both the crystalline and the amorphous phases of polymers. The possibility to analyze all structural phases of a polymer material by only one technique is a significant advantage of Raman spectroscopy compared with traditional methods of polymer characterization, such as X-ray analysis or differential scanning calorimetry (DSC). In the case of copolymers, the amorphous phase structure is especially important, since the crystallinity of these materials is typically low. Raman structural analysis does not require any sample preparation in this case, which is important for preventing the sample structure from changing during processing. The polymer and copolymer structures in the isotropic and deformed states can be explicitly studied by Raman spectroscopy in terms of the chemical and phase compositions (in particular, the degree of crystallinity), the contents of different conformers in the amorphous phase, and the orientational order of macromolecules.

As an example, Fig. 1 depicts a Raman characterization of random ethylene/1-hexene copolymers (CEHs). For the sake of a detailed interpretation, the Raman spectrum of the CEH with 37% of 1-hexene is compared with the spectra of neat PE film, PE melt, and liquid (at normal conditions) n-alkane \( \text{C}_{16}\text{H}_{34} \). A missing line at 1415 cm\(^{-1}\) in the CEH Raman spectrum points to the absence of the PE-like orthorhombic crystalline phase in this copolymer, while the reduction of the intensity of the lines at 1060, 1130, and 1295 cm\(^{-1}\) indicates the decrease in the content of trans-conformers in the CEH. Simultaneously, the growth of the intensity of the shoulder bands at 1080 and 1305 cm\(^{-1}\) is an evidence for the increase in the content of gauche-conformers in the CEH amorphous phase. The analysis of the bands at about 800 cm\(^{-1}\) have evidenced that the CEH structure contains a significant amount of end \(-\text{trans},\text{gauche}\) and \(-\text{trans,trans}\) conformers.

Another example showing a Raman structural analysis of random propylene/1-butene copolymers (CPBs) is presented in Fig. 2. The copolymer spectra are compared with the spectra of low- and high-crystallinity samples of neat isotactic PP, which were synthesized in the presence of two different catalysts. The most significant spectral alterations related to the change in propylene content were observed in the two lines at 809 and 841 cm\(^{-1}\). The 809 cm\(^{-1}\) line corresponds to vibrations of PP isotactic chains in the crystalline phase, while the 841 cm\(^{-1}\) line is associated with vibrations of PP isotactic chains having isomeric defects. Therefore, the Raman data have revealed a reduction in the content of isotactic chains in the crystalline and amorphous phases of the CPBs with the decrease in the propylene content. Based on the integral intensity analysis, we have concluded that the content of isotactic chains in the CPB crystalline phase decreases faster than that in the CPB amorphous phase. The line at 767 cm\(^{-1}\) is due to the formation of sufficiently long butene sequences in the copolymer chain.

The investigations of a number of ethylene and propylene copolymers have led us to the general conclusion that the conformational composition and the phase state of copolymer macromolecules depend on the content and chemical structure of the incorporated monomer and the type of the catalyst used for the synthesis. The conformational and phase order decreases with the increase in the incorporated monomer content, and this tendency is more pronounced with the increase in the size of the incorporated monomer unit. The values of the copolymer crystallinity, determined by Raman spectroscopy, X-ray diffraction analysis, and DSC, are fully consistent, and also explain well the change in the copolymer mechanical properties.

Summing up, in this study, we have demonstrated that Raman spectroscopy can offer a rather versatile approach for a detailed structural characterization of random copolymers of ethylene and propylene.
Fig. 1. Raman spectra of neat PE, recorded at 24 and 136°C, ethylene/1-hexene copolymer (CEH) with 37% of 1-hexene, and the n-alkane C_{16}H_{34}.

Fig. 2. Raman spectra of propylene/1-butene copolymers (CPBs) and neat PP (with crystallinity of 10 and 70%).

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Arrays of silicon nanowires (SiNWs) with mean diameters of about 50–350 nm formed by wet-chemical etching of crystalline silicon wafers were investigated by means of photoluminescence and Raman spectroscopy. The photoluminescence bands in the spectral ranges of 650–900 nm and about 1100 nm were detected and explained by the radiative recombination of excitons confined in silicon nanocrystals at the surface of SiNWs and by the interband photoluminescence in the volume of SiNWs, respectively. The intensities of the interband photoluminescence and Raman scattering under excitation at 1064 nm were significantly larger for the SiNW samples in comparison with that for the crystalline Si substrates. For shorter wavelengths the ratio of Raman signals for SiNW and initial crystalline silicon wafer increases for more ordered arrays of SiNWs of greater diameter and decreases for less ordered SiNW structures. Besides, coherent anti-Stokes Raman scattering was found several times more effective in SiNW ensembles than in initial silicon wafer. These facts are explained by strong scattering of the excitation light, which results in partial light trapping in silicon nanowire arrays.

1. Introduction

Silicon nanowires (SiNWs) attract special researchers’ attention due to their potential use in photonics, photovoltaics, and sensors. For all possible applications controlling the structure, electronic and optical properties of nanowire ensembles is of great importance. A novel SiNW fabrication technique, namely wet chemical etching (WCE) of crystalline silicon (c-Si) wafers in HF-based solutions, resulting in particular in ordered nanowires and their visible photoluminescence (PL) [1] opens up new possibilities for employment of SiNWs with desired parameters in photonic and optoelectronic applications. SiNWs fabricated by WCE demonstrate significant enhancement of Raman and interband (infrared) PL signals in comparison with c-Si [2]. The reason of the effect is likely to be connected with the light trapping in SiNW arrays. That is why it is important to study optical properties of SiNW ensembles in detail paying special attention to their connection with structural parameters.

2. Experimental

Lightly and heavily doped (100) and (111) c-Si wafers were used as substrates for the SiNWs growth. In the first step of the employed WCE method, silver nanoparticles of different morphology were deposited on surfaces of the substrates by immersing them in aqueous solution of 0.02 M of AgNO₃ and 5 M of HF in the volume ratio of 1:1 for 30 sec. In the second step, the c-Si substrates covered with silver nanoparticles were immersed in a 50 ml of the solution containing 5 M of HF and 30% H₂O₂ in the volume ratio 10:1 in a teflon vessel for 1 h at room temperature. The arrays were washed in a concentrated (65%) HNO₃ for 15 min to remove residual silver nanoparticles from the SiNW surfaces. SEM measurements evidence morphology and size of nanowires dependent on initial c-Si wafer doping with SiNW diameter varying from 50 to 350 nm (See Fig. 1).

PL in the spectral region of 600 to 1100 nm was excited by the Ar-ion laser radiation (364 nm). A Fourier-transform infrared (FTIR) spectrometer (Bruker 66/vS) equipped with a Raman module (FRA106/S, cw Nd:YAG laser excitation) was employed for the Raman-scattering and infrared PL measurements. Coherent anti-Stokes Raman scattering (CARS) was detected with a help of the laser system based on a diode-pumped Nd:YVO₄ oscillator with “nonlinear mirror” modelocking and a multipass Nd:YVO₄ amplifier (8 ps, 1064 nm, 2 μJ, 1 MHz). The broadband radiation generated by a part of the fundamental radiation in an optical fiber was collimated and combined together with the fundamental radiation to pump the CARS signal detected in the backscattering geometry in the spectral region from 800 to 1030 nm.

Figure 1: Cross-sectional SEM images of SiNW ensembles, grown on heavily (A) and lightly (B,C) doped c-Si wafers with (100) (B) and (111) (A,C) crystallographic surface orientations.
3. Results and discussions

A broad near-infrared PL band peaking at 1120 – 1150 nm and Raman signal at 520 cm\(^{-1}\) were observed for all SiNW samples and c-Si substrates (Fig. 2a). SiNWs demonstrated more effective Raman scattering and interband PL than initial c-Si wafers. In contrast to c-Si, Raman signal for SiNWs is completely depolarized due to multiple scattering (Fig. 2b). Besides, SiNW ensembles exhibit visible PL, which is absent in c-Si (Fig. 2c); this fact indicate Si nanoparticles formed at the nanowires wall during the etching process.

Enhancement of Raman signal in SiNW ensembles strongly depends on their geometrical structure and exciting-radiation wavelength. As one can see from Fig. 3, the ratio of Raman signals for SiNW ensembles \(I_{\text{SiNW}}\) and initial c-Si wafer \(I_{\text{wafer}}\) strongly depended on excitation wavelength. The rise or fall of the \(I_{\text{SiNW}}/I_{\text{wafer}}\) ratio are determined by size of SiNWs and degree of their order. For the most ordered sample B (Fig. 1b) \(I_{\text{SiNW}}/I_{\text{wafer}}\) increases with the wavelength decreasing, whereas for sample A (Fig. 1a) it decreases; at last \(I_{\text{SiNW}}/I_{\text{wafer}}\) practically does not for vary for C sample, less ordered than B but more ordered than A.

The CARS spectrum collected from the c-Si sample consists of the background and a peak at 1008 nm, corresponding to the resonance with the phonon frequency of Si lattice. The most significant feature of the CARS signal from the SiNW ensembles is that the amplitude of the CARS signal is substantially higher than that from the c-Si.

We attribute the observed effects to light trapping (localization) that can take place in nanowires of the observed size. Decrease of the excitation wavelength enhances both light scattering and absorption effects. A competition between them determines the photon lifetime in SiNW ensembles and, therefore, efficiency of PL and Raman scattering.

Thus, the significant enhancement of the PL, Raman and CARS signals in Si nanowires grown by wet-chemical etching in comparison with the corresponding c-Si substrates is found. The observed effects can be explained by a partial light localization in Si nanowire ensembles because of the strong scattering, which increases the interaction efficiency of the excitation light and Si nanowires.

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References


COUPLING SELECTIVE REACTIONS AND SIGNAL ENHANCEMENT IN DISPERSE SOLUTIONS FOR THE ANALYSIS OF TECHNOLOGICAL AND BIOMEDICAL SAMPLES BY PHOTOTHERMAL SPECTROSCOPY

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The lecture will survey the main trends of research in photothermal spectroscopy related directly or indirectly to analytical chemistry and applied chemical analysis. The advantages and drawbacks of photothermal spectroscopy will be considered. Particular attention will be given to the coupling of photothermal spectroscopy to other analytical techniques, advances over conventional methods. Measurement of biomedical samples and disperse systems will be exemplified. Prospects for the practical photothermal analysis will be discussed.

Photothermal spectroscopy develops in many directions, and since the 1980s, it had been used in various analytical applications, which include highly sensitive photometric measurements and versatile detection schemes in liquid chromatography and capillary electrophoresis. Recently, much attention is paid to the applications of photothermal spectroscopy in microfluidic systems (chemical microchips or µ-TAS), which begin to play a key role in analytical chemistry [1]. However widespread these well-known areas of photothermal applications are, the potentialities of photothermics in analytical chemistry and chemical analysis are even wider.

In this lecture, some examples of new relevant analytical applications based on well-known and novel (selective) photometric reactions will be given, according to Fig. 1. In this lecture, we will show that photothermics shows wide potentialities both for the determining the absorption-band parameters of proteins and for detecting laser-induced photochemical reactions; high precision of the measurements of absorption spectra is observed both in solutions and in cellular structures. For haemoglobin and cytochrome c we estimated the amounts of proteins providing the determination of molar absorptivities and photochemical quantum yields.

We will discuss multispectral photothermal flow cytometry with multiple dyes having distinctive absorption spectra as multicolor contrast agents. As proof-of-concept, we characterized high-speed photothermal flow cytometry [2] capability to monitor the clearance of three dyes in an animal model in vivo and in real time. The possibility for accurate measurements of various dye concentrations were verified in vitro using photothermal and spectrophotometric technique under batch and flow conditions. We further analyze the potential of integrated photothermal flow cytometry.
spectroscopy with multiple dyes for rapid and accurate (≤4%) measurements of circulating blood volume without a priori information on hemoglobin content, which is impossible with existing optical techniques.

As a part of well-known paradigm that photothermal spectroscopy is ‘not just highly sensitive photometry’, the new applications of photothermal spectroscopy are connected with a recent boom in solid-state spectrophotometry [3]. Novel sensible materials (specially designed polymer matrices or surface-enhanced glasses/films with grafted or absorbed photometric reagents) can be used in the form of transparent chips, films, or resins. These materials serve as transducers in novel gas/aerosol/solute optical sensors and in microfluidics and state-of-the-art separation/preconcentration analytical methods. Photothermal spectroscopy is used for a considerable increase in the sensitivity of photometric measurements of such materials. The examples that will be given include trace metal determination, classical and enzyme kinetic indicator systems for phenolic compounds, immunoassays, and nanoparticle-assisted sensible materials. Moreover, lasers can be used for photoinduced synthesis of nanoparticles in polymer matrices with simultaneous online photothermal control.

Another field of application of photothermal spectroscopy is the analysis of heterogeneous materials (solid or liquid), including dynamically appearing and changing heterogeneity. The examples will include the formation of nanoparticles, homogenous formation of crystalline and amorphous residues, the processes of protein crystallization, which can be monitored and analyzed using photothermal techniques. The application of photothermal spectroscopy for the quantification, size estimation, and photochemical processes in heme proteins will be discussed. The examples of multi-wavelength photothermal and photoacoustic imaging and determination of nanodiamonds, fullerenes, and normal sickle haemoglobin [4] in vivo (Fig. 2) will be discussed. Similar methodological approaches are now used for photothermal detection in biologically active systems like cyanobacteria, diatomic algae and other bacterial pollutants in real water systems or bodies, which can be used for early diagnostics of water pollutions.

![Figure 2: Optoacoustic and optical Hb spectra of control mice (nude) and sickle-cell mice (gray) normed at 543 nm, optical spectra corrected for scattering (left) and microscopic photothermal-lens images of normal (upper right) and sickle (lower right) erythrocytes, figures are steps of the scanning system (100 nm).](image)

Finally, some schematics under discussion involve differential schemes and those combining several photothermal methods (with laser and non-laser excitation sources), fluorescence, scattering, photoacoustics, etc., relevant for analytical practice (aerosol analysis, table-top analytical instruments, etc.) will be discussed.

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**References**

LASER INDUCED CONFORMATIONAL PARTITIONING OF KINDLING FLUORESCENT PROTEIN

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Conformational dynamics of biopolymers play an essential role in their function and covers a time scale from femtoseconds up to tens of seconds. Fluorescent proteins serve as ideal models for studies of interaction between protein dynamics and their function on the entire timescale. Even slightest changes in structure result in dramatic change of fluorescent properties of proteins within femto- and picoseconds. Upon absorption of the first photon, the kindling fluorescent protein (KFP) changes its conformation within few hundred femtoseconds, as accompanied by formation of a new set of hydrogen bonds and trans to cis isomerization of chromophore. Within few picoseconds, a new protonated state of the chromophore appears which is characterized by absorption band at 455 nm, and stays in this state in the darkness up to tens of seconds. Variation of pH leads to appearance of the set of fluorescent conformations with different sensitivity to the quenching by blue (405 nm and 475 nm) light. These experimental results prompt us to assume that pH may regulate the conformational changes in the protein by switching between non-fluorescent and several different fluorescent forms.

Introduction

Fluorescent proteins of the green fluorescent protein (GFP) family play a critical role in the creation of new methods of sub-diffraction microscopy and study of dynamic processes in living cells. However, the mechanism of fluorescent properties of these proteins is still not clarified. Photoswitchable proteins are of most interest to the development of methods of microscopy. asFP595 is the first of such proteins has been discovered, which experiences reversible changes between non-fluorescent and fluorescent states under the influence of powerful laser irradiation. According to the protein structures resolved in the X-ray studies for non-fluorescent state of the protein, the chromophore moiety resides in the protein matrix in the anionic form as the trans-isomer.

Two photon photoswitching

Photo conversion is described as the two-photon process, with the consecutive absorption of these two photons. It has been shown that in experiments with femtosecond pulses a major fraction of excited molecules relaxed to the ground state through the conical intersection after the pulse [1], but a small fraction of the relatively short-lived states (picosecond range) is also generated, which in case of absorption of the second photon exhibits a bright fluorescence [2]. One of the key processes is the trans-cis isomerization of chromophore. The reverse process of cis-trans isomerization to the non-fluorescent state in darkness takes tens of seconds. However, when exposed to blue light, fluorescent state disappears almost immediately. When KFP is strongly light-pumped at the green absorption band, the difference spectrum indicates an appearance of absorption bands at 445 nm.

Computer simulation of spectra

Quantum chemistry modeling of KFP properties by computing structure and spectra of a large molecular cluster mimicking the chromophore containing-pocket assuming absorption bands at 445 nm to the neutral form of the chromophore in the trans configuration [3,4]. Inspection of the available crystal structures of asFP595 and its mutants shows that it is possible to consider a tunnel for a proton route from the exterior of the protein barrel allowing protons to reach the spot. The structure and charge of the amino acid residues nearest to the chromophore are important features responsible for shifts in the absorption wavelength thus underlying the strong role of intermolecular interactions when considering properties of the chromophore inside the protein.

Enhancement of fluorescence at alkali pH

Initiation fluorescence of KFP in aqueous solutions by pH variation is another intriguing property of this protein. Evidence to suggest that changes in the protonation accompanied by the trans-cis isomerization of the chromophore, confirm the explanation of the phenomenon of kindling. This isomerization can occur only when you reallocate the hydrogen bonds in the vicinity of chromophore. Thus, both ways of KFP kindling, photo induction and pH-induction must be associated with specific changes in the network of hydrogen bonds around the chromophore inside the protein [5]. The observed absorption band in KFP at 445 nm may assign to the protein conformation with the neutral form of the chromophore and the following status of the nearest residues: unprotonated His197 and protonated Glu215 [4].
Conformational partitioning at alkali pH

Fluorescent form of KFP that appears at alkaline pH is quenched by blue light only partially. A low-intensity radiation results in practically negligible excitation of KFP by 405 nm within the studied pH range. The fluorescent forms of protein absorb only blue light. At the same time, the efficiency of blue light quenching does not depend on power of blue light when power is more than 20 mW. The population of new fluorescent conformations of the protein appears upon increasing of pH and pumping by green light. This fraction is supposed to be split into several fractions; at least one of which is not quenched by blue light and affected by pH variation [5].

Conclusion

Due to such complicated mixture of conformations in aqueous solution it is hard to expect a simple mechanistic explanation of the observed pH dependences by analyzing hydrogen bond networks near the chromophore on the base of single 3D structure of the protein inspired by the crystal X-ray data and molecular modeling. It is necessary to take into account an ensemble of protein conformations fluctuating near the equilibrium state in solution and the key process responsible for behavior of such ensemble may be the well known fluctuation in protein ionization.

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References

MEASURING OPTICAL PROPERTIES ON ROUGH AND LIQUID METAL SURFACES

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For understanding and optimizing laser processing of metals and alloys the optical properties, especially the absorption in function of the temperature of the work piece up to the liquid phase have to be known. There are several approaches to extend the Drude-Model for optical properties of metal to temperature dependence. However, a verification of these models is difficult due to the lack of sufficient experimental data. Even though measuring optical properties with ellipsometry is well established, such measurements on metals and alloys at elevated temperatures up to the liquid state are very challenging. To collect complex refractive index data of different metals and alloys like Al, Ti, Ag, Cu and steel in the solid and liquid state a custom-made high-temperature ellipsometer was used. The instrument is also used to investigate the influence of curved and rough surfaces due to the heating of the samples during the ellipsometric measurements.

1. Introduction
Measurements of optical properties of metals for the infrared and far infrared region [1][2][3] at room temperature are in general compared with the Drude model [1][2]. There are reports on extending the Drude-Model to different temperatures [4]. Unfortunately experimental data for temperature dependence of the optical properties are only reported for few metals like tungsten or gold [5]. In addition these reports show that it is difficult to correlate the experimental data to theoretical models. In general two or more fitting parameter are involved. Therefore it is necessary to know the optical properties of hot and liquid metals for each single metal of interest as it is not possible to derive these parameters from a model. The goal of the work presented here is to clarify this uncertainty by means of temperature dependent ellipsometry.

An effect that cannot be neglected if temperature-dependent ellipsometry is performed is the fact that due to heating and melting the metal surface is changing constantly its structure and topology. As ellipsometry (i.e. measuring the changing the polarisation of a reflected light beam depending on the optical properties) is highly surface sensitive it is of great importance to know and control this surface changes. Even though there are several approaches to deal with rough surfaces, they seem to fall short when applied to metallic surfaces. On the other hand ellipsometric measurement might be used to quantify the degree of surface finishing [6].

2. Experimental Setup
For measuring the optical properties a standard Rotating Compensator Ellipsometer (RCE)[7] configuration has been used, where the compensator is placed after the sample and before the analyzer (PSCA-setup). A Superluminescent Light Emitting Diode (SLED) with a centre wavelength at 1070nm and a bandwidth of 100nm as a light source and a spectrometer as a detector have been chosen. The ellipsometer is mounted to a vacuum chamber allowing measurements at 10^-5 mbar as well as under an inert gas atmosphere. With the current configuration angles of incidence of 80°, 70°, 45° and 40° for the ellipsometer can be chosen. The samples can be heated in two ways: firstly with a translatable and tiltable heating stage, on which the sample is positioned and with which temperature up to 1000°C could be achieved. Secondly the light of a fiber coupled high power diode laser with a maximum optical output power of 350W is focused onto the surface of the sample. By using both heating methods amongst others steel and titanium can be heated above their melting points of 1450°C and 1670°C, respectively.

3. Experiments and results
3.1 Topology
As mentioned above, ellipsometry data is very sensitive to surface topography. Therefore the influences of surface topology and changes in surface roughness due to elevated sample temperature have been studied. One specific challenge is the influence of a curved sample surface. When melting the metal samples they take a curved, convex or concave shape. Therefore the influence of curved surfaces on the ellipsometry measurements has been studied by doing measurements on steel metal rods and ball bearings of different diameters. It is found that this effect can be well managed as well as the aspect of selecting well suited crucible materials in order to optimize the wetting behaviour of the liquid metal sample and to minimize the metallurgic reaction between the sample and the crucible material. Another important topic is the influence of the evaporation of material from metals and alloys at high temperatures, respectively. In order to avoid strong deposition inside the vacuum chamber walls and the viewports for the ellipsometer and the heating laser, it is found that experiments have to be done under argon atmosphere of about 5mbar.
A quite critical issue is the formation of a contamination layer on the liquid samples. This layer - probably formed by impurities of the samples diffusing to the surface - may strongly influence the ellipsometer data and has to be avoided. Several strategies to minimize these layers will be presented.

Despite several approaches to take the surface roughness into account when doing ellipsometry no satisfactory approach for rough metal surfaces is known. Therefore the influence of the roughness has been studied experimentally in order to estimate its effect on the ellipsometric results. For generating different roughness polymeric substrates have been plasma-treated for a different period of time. Afterwards the substrates have been coated with a 60nm silver layer which conserved the roughness of the polymeric surface. In this way silver layers with roughness values $R_a$ from 4nm to 59nm have been measured. The results in figure 1 on the left show, that the roughness has a strong influence on the measurement of the correct complex refractive index. However, up to $R_a=12$nm the values more or less agree with values of bulk silver reported in literature [8] and show only small dependence on the roughness. For higher values for $R_a$ the roughness impedes a correct measurement of the complex refractive index. At the same time the measured error increases as well.

![Figure 1: On the left: refractive index n (diamonds) and absorption index k (square) as a function of the roughness value $R_a$, literature values [8] for n (point bar line) and k (dotted line). On the right: n and k in function of the temperature.](image)

### 3.2 Temperature dependence

As for the temperature domain below the melting point, the measured values for the complex refractive index show a small dependence on the temperature (e.g. silver, shown in fig. 1 on the right). However, these small deviations are similar to the ones induced by varying roughness. Therefore the variations could be an effect of the growing surface roughness during heat treatment, which can be observed by eye. Furthermore in the case of steel in the temperature region between 600°C and 1000°C a variation of the optical properties due to the appearance of annealing colours could be observed.

As for the domain within the range of the melting point, a significant change in optical properties for the transmission from solid to liquid for several metals including aluminium and steel are reported [4]. With the presented method, such an increase of the refractive index and absorption coefficient from solid to liquid phase could be seen for copper and stainless steel as well, whereas in the case of silver no increase could be measured. Never the less a satisfying theory which explains this effect is missing. To gain additional information, further investigations e.g. titanium from room temperature up to the liquid phase will be done.

### References

Near-infrared spectrophotometry (NIRS) and imaging (NIRI) are quickly growing methods to non-invasively study human tissue using near infrared light, which penetrates tissue several cm deep. The method is appreciated by patients and researchers, because it is quantitative, measures continuously, is painless, can be used at the bedside, is relatively inexpensive and can easily be combined with other modalities such as e.g. fMRI and EEG. Light absorption and scattering of tissue are measured at multiple wavelengths and the concentration of constituents of tissue such as oxyhemoglobin, deoxyhemoglobin are quantified. These physiological parameters are clinically important, because they represent e.g. blood volume, flow and oxygenation and enable to monitor the function and oxygenation of biological tissue. Multiple light source and detector combinations produce images of whole tissue areas. There are many potential clinical applications of NIRS/NIRI. The talk will focus on the application of NIRS/NIRI to study the brain. The talk will be concluded by a vision of future applications and research.

1. Introduction and aims

Near-infrared spectrophotometry (NIRS) and imaging (NIRI) are quickly growing methods to non-invasively study human tissue using near infrared light. One particular focus of studies is brain research. The aim is to give an introduction into the technological aspects of NIRS/NIRI, give an overview of studies of the brain using NIRS/NIRI and conclude with an outlook into the future.

2. NIRS and NIRI technology

In the visible light range, light does not penetrate tissue deeply, because the haemoglobin absorbs light strongly. In the infrared range, water becomes strongly absorbing. But near infrared (NIR) light penetrates tissue deeply (several cm deep), because neither water nor haemoglobin absorb strongly in this range. Haemoglobin is still the main absorber in the tissue in the NIR, which enables to measure the tissue oxygenation. The latter is an important biomarker, because oxygen is vital and the oxygen consumption of tissue depends on its function. Since bone does not contain much haemoglobin, it can be easily penetrated by NIR light and this enables to study the brain non-invasively. Several types of NIRS/NIRI instruments take advantage of this fact. Principles of instruments will be described. The most simple instrument consist of a light source with two wavelengths (one for oxyhaemoglobin (O$_2$Hb) and one for deoxyhaemoglobin (HHb)) and one detector, which is placed at approximately 3cm distance from the light source. Both are placed on the skin of the head above the area of interest in the brain. Thus, changes in blood concentration in the respective area can be quantified based on the diffusion approximation of light transport through tissue (for a review of theory and technology see [1]).

3. Functional brain studies

When the brain is activated by stimulation (e.g. finger tapping for the motor cortex, flashing lights for the visual cortex), it consumes more oxygen. Oxygen consumption is coupled to blood flow by neurovascular coupling. This means that the blood flow increases immediately to supply more oxygen to the activated brain region. The increase in blood flow is overwhelming and consequently results in a net increase in oxygen availability in the activated brain area, despite the higher oxygen consumption. In NIRS/NIRI measurements this is represented by an increase in O$_2$Hb and a decrease in HHb concentration (Fig. 1).

Due to the favourable properties of NIRI, i.e. because it is quantitative, measuring continuously, painless, and bedside applicable, it can also be used for studies of functional brain activity in groups of subjects, where other methods are not available, e.g. in preterm infants, neonates and young children. These studies give valuable information on the development of the brain and different cognitive abilities (for a review see [2]). Besides this fundamental neuroscience research, work is under way to introduce NIRI as a diagnostic tool into clinical application. NIRS/NIRI is also applicable in adults, where it is again employed to study normal brain function and has proven to be an excellent research tool with many potential clinical applications. One example of such an application is rehabilitation after stroke or head trauma. It is expected that rehabilitation is more effective, when the patients actively participate during physiotherapy by mental imagery of their movements. This will lead to a stimulus from two sides, the movement of the limb and the mind. NIRI studies show that mental imagery of movements leads to similar activation patterns like actual execution of the movement [3]. Although the amplitude is smaller during mental imagery compared to motor execution, the size of the activation can be increased by giving feedback [3]. Thus, work is under way to develop NIRI into a system that is able to provide this feedback online.
A functional response to finger tapping. A subject was tapping fingers from 20s to 40s (shaded area left) and resting from 0s to 20s and from 40s to 60s. During finger tapping the $O_2$Hb concentration increases clearly, while the HHb concentration decreases. This is a typical response for brain activation and it is visible in all four channels of the NIRI sensor. The sensor includes four source detector pairs, which are arranged vertically. The sensor was placed on the motor cortex as shown in the diagram to the right.

In addition, this mental imagery of movements, if it can be detected reliably, could be used to trigger external device such as prosthetic devices. NIRI as a brain computer interface has the advantage, that it is easily portable and unobtrusive, i.e. we have been able to produce wireless NIRI devices, which only weigh 40g [4].

4. Brain oxygenation studies

NIRS is also able to determine the oxygen saturation of tissue ($StO_2$) non-invasively and quantitatively [1]. This corresponds to the percentage of haemoglobin that is carrying oxygen. This is a potentially highly useful measure of oxygenation of the brain, because the brain is very sensitive to lack of oxygen. In particular intensive care patients are likely to benefit from NIRS in the future, because they are often unconscious and mechanically ventilated. In neonatal intensive care, NIRS is thus on the verge of entering clinical routine application (for a review see [5]), e.g. to determine whether low blood pressure needs to be treated to maintain $StO_2$ of the brain at sufficient levels [5]. The same is true for adult patients during anaesthesia or in intensive care.

5. Outlook

In the future NIRS/NIRI will enter many clinical studies, where its clinical usefulness will be thoroughly tested. It is expected that many patients will profit from it. In addition the technology will be further developed, i.e. 3D imagers similar to ultrasound scanners will become available, except that they will image haemoglobin concentration and oxygenation, NIRS/NIRI will be miniaturized and included in clothes thus becoming a wearable, comfortable, unobtrusive, diagnostic tool.

6. References

The behavior of some proteins and enzymes in water solutions in the presence of different toxic metals ions were investigated. Interaction of the proteins and enzymes in solutions containing heavy metal ions results in the formation of large (nanosized) clusters. The molecular mechanism of nanoparticles formation are considered in terms of dipole-dipole and charge-charge interaction of the proteins.

Laser light scattering method, photon correlation spectroscopy and polarized fluorescence were used for intermolecular interaction study of the ions with large ionic radii like Pb^{2+} (1.2 Å), Rb^{+} (1.47 Å), Cs^{+} (1.65 Å), Eu^{2+} (1.33 Å), Gd^{3+} (0.98 Å) and some proteins and enzymes in water solutions at the very low concentrations of the salts.

The interaction of the metal ions with the charged surface of the protein in the solution is studied by the measurement of the light scattering coefficient along with the concentration variation of the former.

The ions with large ionic radii presence in the water solutions of some proteins and enzymes like albumin, gamma globulin, pepsin, collagenase, lysozyme, creatin cense and so on stimulate the forming of nanoparticles with the mass more than molecular mass of macromolecules M_o. This effect was confirmed by AFM methods as well. It was observed that the process of nanocluster formation begins at very low concentrations of heavy metal ions about MPC (maximum permissible concentration).

The dependence of masses of the scattering particles on the ionic strength and pH of the solution shows the Langmuir sorption process which leads upon the monolayer saturation to the dipole cluster formation.

The nanosized clusters form as a result of the phase transition when the Coulomb repulsion forces diminish and the pure dipole attraction forces take over.

The appearance of the aggregates can violate metabolic processes in the organism (cells, membranes, blood). That can explain high toxicity of heavy metal for living organisms at rather low concentrations and “poisoning” effect on enzymes and proteins.

Fig. 1 shows the dependence of the relative mass of scattering particles on the ionic strength of the solution. The curve possesses a small slope rise of the relative mass. The ionic strength values in the range from 0.05 mmol/kg to 0.17 mol/kg relate to the process of monolayer formation which takes place until the Langmuir saturation is achieved.

As graph data shows that the scattering particles masses are more than 20 times greater than the mass of the albumin molecule. It depicts the process of the formation of the larger particles which appear to be the nano-sized clusters generated by a number of the original macromolecules. With the presence of Pb^{2+} ions in the solution the cluster formation process occurs at the ionic strength values of 0.15 mmol/kg.

![Figure 1: Dependence of relative mass from ionic strength of albumin solution with Pb^{2+} ions (pH=7.5).](image_url)
A method of treatment microbe nature disease using multiwave laser radiation

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Multiwave laser medical device "Livadia" has been developed for bactericidal and therapeutic impact on the affected organism parts. This device is on the diode pumped solid-state laser and main wavelength radiation conversion 1064 nm into the second harmonic 532 nm and fourth harmonic 266 nm. It has been shown that UV radiation on the wavelength 266 nm on bronchia mucosa with various inflammation types improves regenerative processes in bronchia tissues which decreases treatment deadline.

Multiwave laser medical device "Livadia" has been developed either for bactericidal or for therapeutic impact on the affected organism parts [1,2]. This device is on the diode pumped solid state laser and main wavelength radiation conversion 1064 nm into the second harmonic 532 nm and fourth harmonic 266 nm.

We have shown experimentally that the vanadate a-cut σ-polarized laser has the best parameters for the passive Q-switch with Cr⁴⁺:YAG. The features of the laser action, in this case, was investigated. Our laser has polarized radiation with the peak power of 17 kW on 1.06 µ. Excellent laser parameters allow effective conversion into the second and fourth harmonics, even outside the laser cavity. We have obtained 100 mW on the second and 5 mW on the UV laser radiation fourth harmonic with pumping power about 4 W. The set of vanadate crystals was investigated as an active medium for such lasers.

Parameters of “LIVADIA” medical device:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength of radiation</td>
<td>1064 nm</td>
</tr>
<tr>
<td>Mean power</td>
<td>300 mW</td>
</tr>
<tr>
<td>Radiation frequency</td>
<td>10-20 kHz</td>
</tr>
<tr>
<td>Impulse duration</td>
<td>3 – 10 ns</td>
</tr>
<tr>
<td>Radiation outlet</td>
<td>optical fibre</td>
</tr>
<tr>
<td>Exposition time</td>
<td>0.1-100 min</td>
</tr>
<tr>
<td>Use power</td>
<td>400 W</td>
</tr>
<tr>
<td>Size</td>
<td>340x250x150 mm</td>
</tr>
<tr>
<td>Weight</td>
<td>8 kg</td>
</tr>
</tbody>
</table>

Nearly 10% tuberculosis patients have bronchia tuberculosis (its treatment has the same difficulties as lung tuberculosis does). To transport the radiation by means of light guide is very comfortable. It realizes the affected spots of bronchia and trachea. Treatment procedure is followed by: a light guide which is brought into the channel of bronchoscope. It is used for biopsy and then slowly taken out together with bronchoscope from bronchi and trachea. This procedure lasts 60 – 90 sec.

Therapeutic effect of the device use is achieved by multiwave radiation function in UV, visible and IR wavelength ranges[3]. There is the opportunity to use either separate wavelengths or their combinations that allows choosing the most optimal radiation regime for each certain disease. Combined radiation effect can be used for endocavernous treatment of destructive lung tuberculosis forms. The alternative region use is purulent-inflammatory soft tissue processes treatment. Combined radiation effect in soft tissues causes pathogenic microorganisms growth inhibition and simultaneous stimulation in reparative tissue processes. That is very actual in gynecology, otolaryngology, therapy and especially in purulent surgery.

References

THE LASER FLUORESCENCE ANALYSIS METHOD USE FOR EXPRESS-DIAGNOSIS OF ANTIBIOTIC RESISTANCE

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The adequate antibiotic method choice is being developed with the laser fluorescence analysis blood plasma method with laboratory-diagnostic device "Spectrolux-MB" use. It is used the microorganisms ability and products of their vital functions to fluoresce with laser radiation use in depending on features and physiological process activity in them. The fluorescence analysis method has great prospects in urgent surgery and other medicine branches due to its high information contest, low cost (compared with other methods of express-diagnostics) and information obtaining speed.

The development of adequate method of antibiotic choice is reported using the laser fluorescence analysis of blood plasma with the laboratory-diagnostic device "Spectrolux-MB" [1]. The method is based on the ability of microorganisms and products of their vital functions (metabolism) to fluoresce under laser radiation. The method of fluorescence analysis has great prospects in urgent surgery and other medicine branches due to its high information content, low cost (compared to other methods of express-diagnostics) and high speed of information acquisition [2].

The choice of the effective antibiotic is obtained by the following way: microflora is supposed to be sensitive to the antibacterial preparation if there is normalized fluorescence intensity decrease more than 20% under its activity. For antibiotic resistant microflora the fluorescence intensity of blood plasma does not change within the time or increases with respect to the control spectrum. In this case it is necessary to correct the concentration of input preparation or to replace it.

The express-method for the antibiotics efficiency determination by laser fluorescence diagnosis of blood plasma has been offered. The clinical trials of the method have been carried out. The conducted prospective research with fluorescence diagnosis method allowed confirming the mixed infection in 86% cases, as well as the microbiological exudate seeding results were not informative in 46% cases among these patients. The clinical efficiency of conducted antibacterial therapy with the fluorescence plasma results was achieved in 74% cases (excluding the patients with developed complications). This allows considering the method as the promising direction in the optimal antibacterial therapy development among patients with abdominal sepsis and demands to carry on some researches for the further increase of efficiency.

The fluorescence analysis method of antibiotic efficiency has shown its productivity and significance among the patients with pyoinflammatory infection in the abdominal surgery. It was confirmed microbiologically and clinically. The method allows matching adequate and effective chemotherapy within 3-4 hours since the patient checking-in the hospital. Standard microbiological analysis usually requires 2-4 weeks. Therefore, LIF of blood plasma has enormous advantage over classical method. It improves the treatment results and decreases the patient staying in the hospital.

References


RAMAN STUDY OF STRUCTURE OF ORGANIC LAYERS IN ALKYLAMMONIUM/CLAY HYBRIDS

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We demonstrate the potential of Raman spectroscopy for quantitative characterization of organic layers within nanogalleries with confined geometry in alkylammonium/clay hybrids and discuss the phenomenon of the splitting of the band at about 1130 cm\(^{-1}\) in the Raman spectra.

The incorporation of alkylammonium surfactants into clays leads to interesting hybrid systems (modified clays), which are used as fillers for polymer/clay nanocomposites and as models for biomembranes. The intercalated alkylammonium ions of such surfactants undergo self-reorganization and form own organic layers between the silicate plates of clay crystallites. Real-time structural characterization of the CH\(_2\)-chain conformational and packing order of these organic layers is of great importance, because these characteristics strongly depend on the chemical composition and content of the surfactants, as well as on the production parameters of the surfactant/clay hybrids. Currently, modified clays are extensively studied by several methods, which include X-ray diffraction and differential scanning calorimetry, IR-spectroscopy, and computer simulations. However, these methods are limited to the characterization of the conformational and packing order of the organic layers in alkylammonium/clay hybrids.

In this contribution, we present micro-Raman scattering investigations of clay (Na\(^+\)-montmorillonite, MMT) modified by a number of alkylammonium surfactants, including DDAB \([\text{CH}_3(\text{CH}_2)_{13}-\text{N}(\text{CH}_3)_2\text{Br}^-]\), CTAB \([\text{CH}_3(\text{CH}_2)_{15}-\text{N}(\text{CH}_3)_3\text{Br}^-]\), DODAB \([\text{CH}_3(\text{CH}_2)_{18}-\text{N}(\text{CH}_3)_2\text{Br}^-]\), and a combined modifier DODAB-CTAB. We demonstrate that the monitoring of the Raman bands at approx. 705, 1060, 1080, 1300, and 1440-1460 cm\(^{-1}\) allows real-time, non-destructive quantitative sensing of the conformations and packing order of the modified clay. Also, we put emphasis on a very interesting and unexpected behavior of the band at ~ 1130 cm\(^{-1}\), which corresponds to the symmetric C-C stretching vibrations in \textit{trans} segments, seen in the Raman spectra of such surfactant/clay hybrids. We have observed that the shape, width, and peak position of this band strongly depend on the chemical composition and content of the alkylammonium modifier in the clay. For instance, Fig. 1 demonstrates the behavior of this band in the Raman spectra of some alkylammonium compounds under study. We have shown that at least two types of \textit{trans} segments contribute to the envelope of the bands at ~ 1130 cm\(^{-1}\). These two types of \textit{trans} segments appear as the result of bending of CH\(_2\) chains in alkylammonium compounds and differ in their chemical compositions. The \textit{trans} segment of the first type consists of a sequence of CH\(_2\)-groups with terminal (CH\(_3\))\(_n\)-N- unit. The \textit{trans} segment of the second type contains only CH\(_2\)-groups. We have found that the Raman shift of the symmetric C-C stretching mode differs for these types of segments. Monitoring the peak positions of the two sub-bands assigned to the different types of \textit{trans} segments allows determining their lengths. We use the Raman data containing the information about the types and lengths of the \textit{trans} segments in the modifier molecules within the clay interlayer space to validate and improve mathematical models of the structure of modified clays.

Fig. 1. Behavior of the C-C stretching mode in the Raman spectra of alkylammonium compounds under study.

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SENSING COCAINE IN SALIVA WITH A QUANTUM CASCADE LASER (QCL)

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Sensing of drugs like cocaine and heroin in body fluids, particularly in saliva, is of great interest. Current methods are often not quantitative enough or need sophisticated sample treatment. We present two new optical methods based on a simple one-step extraction, a mid-infrared quantum cascade laser and measurements either by Attenuated Total Reflection (ATR) or direct transmission. The current limit of detection is around 9 µg/ml (ATR) or < 1 µg/ml (transmission). Work on combining the QCL with waveguides and microfluidics is in progress. This enables a miniaturization in a view of a portable device and should allow a substantial reduction of the LOD towards the limit required by law of ≈ 20 ng/ml.

1. Introduction

The nano-era project IrSens [1] aims to build a platform with the potential to be miniaturized to detect traces of molecules in liquids. The detection of cocaine in saliva serves as a demonstrator for the feasibility of the project. Drug detection is important since driving under the influence of drugs is a major problem in many countries. Therefore reliable, portable and cost-effective tests are needed.

Many techniques have been applied to detect cocaine in body fluids like for example immunoassays (limit of detection (LOD) 20 ng/ml) [2], Gas or Liquid Chromatography combined with (tandem) Mass Spectroscopy (GC- or LC-MS/MS), (LOD 1 ng/ml) [3], aptameric sensors (LOD 3 µg/ml to 121 µg/ml) [4,5], surface enhanced Raman Spectroscopy with metal doped sol gels (LOD in the range of µg/ml) [6].

The above mentioned methods have either limited reliability [2,7], require extensive sample preparations or lack portability. We introduce a technique that yields comparable detection limits with a very simple one-step-extraction method and infrared detection. Two approaches have been realized, one employs direct transmission on the solvent used for the extraction of the saliva sample. The second approach utilizes Attenuated Total Reflection Spectroscopy (ATR) for analyzing the dried extract from the saliva. Our one-step extraction preparation technique is simple and does not require bulky or expensive equipment. In fact Wägli et al. demonstrated that the technique is feasible with a microfluidic device using similar liquids [8].

2. Implementation, Results and Discussion

2.1 Implementation

Extensive prestudies implied that the absorption lines of cocaine with the least interference from saliva or other possible substances like diluents, adulterants, masking substances and common products like soft drinks are around 5.7 µm [9].

ATR data were recorded with a standard commercial ATR block with exchangeable ZnSe top-plates (11 to 12 reflections) integrated in a QCL set up. The ATR unit also fits into the FTIR spectrometer Paragon 1000 PC (Perkin Elmer) which was employed for additional reference measurements for the confirmation of the selectivity of the process. The direct transmission measurements were performed with a 1 mm transmission cell (Perkin Elmer) with windows of CaF₂ and NaCl.

We use a Quantum Cascade Laser (QCL) around 1750 cm⁻¹ (5.7 µm) with a tuning range of approximately 10 cm⁻¹ [1] and two MCT infrared detectors (Vigo System S.A.). The optical set up consists of a reference and sample beam, which pass either through the ATR unit or the transmission cell (cf. Fig. 1). This allows compensation of laser fluctuations. For even more precise measurements the solvent is measured regularly as a reference.

The acquired saliva sample is filtered with syringe filters (0.2 µm Sarsted). Afterwards the cocaine is dissolved in the saliva. Then the one-step extraction method is performed which is done by one person only and takes less than 5 min. The details of the extraction method will be published elsewhere.

Figure 1: QCL set-up. After collimating, the laser beam is split into the reference and sample beam. The sample beam passes either through the ATR unit or the transmission cell whereas the reference beam is focused directly onto the detector.
2.2 Results and Discussion

The transmission measurements yield a detection limit of cocaine concentrations in the solvent of < 1 µg/ml (Fig. 2a). The ATR measurements yield currently slightly higher limits which is not due to the technique as such but rather due to the set path length within the ATR crystal. These concentration limits should be put into perspective with actually found concentrations in saliva which can range up to 450 µg/ml depending on the form of administration of the drug, the amount and the person itself [10]. Therefore the linearity of the signal in this regime was investigated. The absorbance of cocaine measured in the solvent dried on the ATR crystal is displayed in Fig. 2b. Good linearity is achieved.

The displayed measurements suggest that the combination of infrared spectroscopy with a simple one-step extraction method yields limits of detection comparable to alternative optical methods with the advantage of easy sample preparation and the potential for miniaturization.

3. Outlook

The next step is to integrate a waveguide and a microfluidic system [1] into our set-up. This approach is expected to lower the limit of detection substantially due to the excellent coupling of the evanescent field with the liquid and the simplified sample delivery.

The one-step-extraction technique in combination with infrared spectroscopy can also be adapted for other substances. Successful first experiments have been done on the detection of caffeine in several caffeine containing beverages like black or white tea, coffee or a suspension of water and Guarana. The determination of the caffeine content of drinks with a portable sensor could support Alzheimer and Parkinson studies that investigate a possible correlation between caffeine consume and the prevention of these diseases [11].

References

In this manuscript, we introduce the application of optical coherence tomography as a dosimetry and therapy control in sub-threshold retina therapy and discuss the need for a high axial resolution. We present a method to improve the contrast and the axial resolution of frequency domain optical coherence tomography signals using the Maximum-Likelihood deconvolution algorithm. We investigate the influence of the system point spread function on the performance of the algorithm, and the improvement in signal to noise ratio and axial resolution of the Optical Coherence Tomography signal and show improvements of axial resolution on simulated data by a factor of 4-5 and a factor 1.5-2.5 on real data. Lastly, we illustrate the effects of the algorithm qualitatively and quantitatively on real data from both artificial samples and pig eye retina.

1. Introduction

Ever since optical coherence tomography (OCT) was first described in 1991 [1], it has proved to be a very useful and important imaging modality for non-invasive and high resolution mapping of different biological structures and tissues. However, for certain fields of application the currently available axial resolution is scarcely sufficient to enable meaningful imaging. One of those applications, the employment of OCT for the monitoring of laser lesions caused by the Selective Retina Therapy (SRT) [2] in the retinal pigment epithelium (RPE), is currently under investigation. During SRT monitoring, the RPE cell monolayer with a thickness of between 20 and 30 µm will be scanned. It becomes evident that for a reliable detection of lesions in the RPE layer, axial resolution of at least 2-3 µm is required.

Currently, most of the high axial resolution systems are realized using cost-intensive femtosecond lasers [3]. If a superluminescent light emitting diode (S-LED) light source is used, the technical complexity of the OCT system noticeably increases with larger source bandwidth. However, the known point spread function in OCT represents a possible starting point for methods such as the Maximum-Likelihood deconvolution algorithm, aiming to improve the resolution on the post-processing rather than the hardware side.

2. Measurement System and Methods

2.1 OCT System

For the acquisition of the OCT sample data, two independent systems operating with light source spectra in different wavelength regions have been used. Both systems are custom-made FD-OCT systems designed at Berne University of Applied Sciences and equipped with light sources using superluminescent light-emitting diodes (S-LED). Both spectrometers feature a 12-bit CCD line camera. Both sample arms are equipped with two galvo scanning mirrors and a telecentric achromatic doublet lens system. The incident power at the sample arm was kept at constant value.

2.2 Maximum-Likelihood Algorithm

The Maximum-Likelihood algorithm used for this work is based on the work of Kormylo and Mendel [4]. The version of the algorithm implemented in this manuscript is described in [5]. The algorithm can be written as

\[ \hat{g}(x) = h(x) \otimes \hat{s}(x) \]

\[ \hat{d}(x) = \frac{g(x)}{\hat{g}(x)} \]

\[ r(x) = \frac{1}{H(0)} \cdot h(-x) \otimes \hat{d}(x) \]

\[ \hat{g}(x) = h(x) \otimes \hat{s}(x) \]

\[ \hat{s}(x) = \hat{s}(x) \cdot r(x) \]

In the algorithm described in Eq. (1), \( \hat{g}(x) \) is the updated estimation of the original image after k iterations, \( \hat{d}(x) \) is the updated intermediate image, \( h(x) \) is the known point spread function, \( \hat{s}(x) \) is the estimated original image convoluted with the known point spread function, and \( H(0) \) represents the integral over the point spread function.

The Maximum-Likelihood algorithm shown in Eq. (1) takes the estimation of the original image, convolutes it with the known system PSF and creates a point-wise correction vector by comparing the result with the measured data and back projecting the normalized vector into object space. The estimated image is then updated with the correction vector and the next step of the iteration starts until the defined convergence is reached. It is assumed that the algorithm performs
better concerning side-lobe suppression rather than general reduction of peak width. Therefore, the shape of the PSF is supposedly of big influence on the algorithm performance.

2.3 Sample Data
The algorithm was tested on OCT data from artificial samples consisting of scotch tape, paper and microscope cover slip as well as from ex-vivo pig eye retina. For the measurements, fresh porcine eyes with detached anterior segment were placed in a specially designed sample chamber and imaged with the OCT system.

3. Results
The presented deconvolution algorithm was applied to datasets of OCT scans taken from the artificial scotch tape and glass sample and the dissected porcine eyes. Two independent systems with different source spectra were used to illustrate the effect of the PSF on the algorithm performance. Fig. (1) shows a close-up of the OCT image of the artificial sample where the gain in axial resolution can be seen clearly, as well as OCT images from porcine retina, with the gain in resolution and SNR indicated by the corresponding Ascans.

For the 800 nm high-resolution scans (a) and (b), the full width at half maximum (FWHM) of the analyzed signal peak decreased from approximately 4.8 \( \mu \text{m} \) to 2.2 \( \mu \text{m} \) whereas the signal-to-noise ratio (SNR) improved from 39.35 dB to 46.5 dB. For the 1060 nm scans, the FWHM of the analyzed peak decreased from 8.6 \( \mu \text{m} \) to 5.1 \( \mu \text{m} \) and the SNR increased from 43.44 dB to a value of 48.29 dB. Concerning the ex-vivo pig eye retina OCT, the data sets feature a significantly lower SNR than the sets from the artificial samples which led to a more prominent noise floor. In contrast to the scans presented in other publications, no averaging was performed on the datasets presented in this manuscript. The corresponding Ascans are displayed in subplots (c) and (d). The FWHM of the signal peak dropped from approximately 6.3 \( \mu \text{m} \) to 3.6 \( \mu \text{m} \) while the SNR increased from 16.1 dB to 22.32 dB.

4. Conclusion and Outlook
In this manuscript, we were able to support the hypothesis that the deconvolution algorithm shows noticeably better performance in the case of a well-structured source spectrum and a resulting point spread function including side lobes. As practically every S-LED light source with a bandwidth of more than 50 nm needs to combine multiple S-LED modules to achieve the required spectrum, such a structured spectrum is usually present in all OCT systems operating with broadband light sources. For further developments and for real-time applications, an assessment of the convergence criteria and a speed-up of the algorithm will be crucial. However, results show that the algorithm works stable with real sample data and suggest that the algorithm is capable of improving image quality in the dedicated application field.

References
1. Introduction
Erbium (Er) doped materials are of great interest for optoelectronics because of their emission at 1.54 µm, which correspond to the standard spectral region of the modern optical communication systems [1]. It is known that the photon cutting effect can be the probable excitation mechanism of RE ions which was predicted by Dexter [3]. It consists in the splitting of the excitation energy of one nanocrystal and transmission it to two RE-ions simultaneously. In our work we introduce a method based on the formation of por-Si, which is used as a solid matrix to introduce rare earths (RE) as Er and Yb.

2. Experimental results and discussion
Samples of porous silicon (porSi) were prepared by standard electrochemical etching of c-Si wafers in a solution of HF and C₂H₅OH. After etching they were soaked with a solution of RE in sulfuric acid. Then the samples were annealed in air at different temperatures varied from 600 to 1100 °C for 1 hour.

Photoluminescence spectra of the Er-doped samples (Fig. 1) exhibit a complex structure with a broad line at 750 nm related to the intrinsic emission of por-Si and several lines at 850 nm, 990 nm and 1530-1560 nm of Er³⁺. Also there is a broad line at 1507 nm, which corresponds to the defect-related luminescence [3]. A sharp line of Yb³⁺ near 980 nm was found in Yb-doped samples.

The electroluminescence spectrum of por-Si:Er was found to consist of mostly the defect-related line at 1500 nm.

Figure 1 Typical PL spectrum of a por-Si:Er

To understand the excitation mechanism of RE (the quantum cutting effect or the single quant energy transition) we measured pump power dependencies of the PL intensities. A model of these processes based on rate equations was applied to analyze the experimental results. A signature of the photon cutting effect was revealed in the samples of por-Si:Yb, which can be used in photovoltaic applications.

References
LASER DIAGNOSTICS OF PHOTOLUMINESCENT PROPERTIES OF SILICON AND SILICON CARBIDE NANOCRYSTALS

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Our work is devoted to investigate new types of system based on silicon and silicon carbide nanocrystals in semiconductor matrices, which possess both efficient luminescence and electrical current injection.

Samples of the first type were prepared by rapid thermal annealing of amorphous silicon layers (a-Si:H) and subjected to stain etching in hydrofluoric acid solutions. Samples of the second type were prepared by direct deposition of carbon and silicon atoms on c-Si substrates by using arc discharge [1].

Firstly, it was shown that nc-Si can be prepared by rapid thermal annealing and stain etching of a-Si:H. The photoluminescence (PL) spectra of nc-Si/a-Si:H layers represent a strong emission band in the region of 600-900 nm similar to the PL band of porous silicon used for comparison.

At second, ion beam deposition on silicon substrates allows to produce nanocomposite films consisted of silicon and silicon carbide nanocrystals. The films exhibit both “blue” (400 – 500 nm) and “red-infrared” (600 – 1000 nm) PL bands, which are attributed to the radiative recombination of bound excitons on defect states in silicon carbide nanocrystals and silicon nanocrystals, respectively.

In conclusion, the obtained results indicate new possibility for preparing Si-based luminescent films, which can be used in light-emitting devices.

References:
We have realized the laser treatment modes that can be used in order to form nanoporous structures in Cu-Zn system alloy. The exposure to periodic laser pulses with the pulse-repetition rate up to 4000...5000 Hz – provided that the material is being heated below the melting point – makes it possible to produce a steady stress on the sample surface. The proposed patented technology is promising for manufacture of catalysts and ultrafiltration membranes.

1. Introduction
Nanoporous materials are used in filtration of gases and liquids in medicine, nuclear power engineering, microbiology, food industry and other [1-4]. The most commonly used membranes are made of nanoporous materials based on polymers, glass, ceramics and graphite. Compared with them, metal membranes have superior technological and physical-mechanical qualities, such as: mechanical durability, heat resistance, they have a long period of operation, can be cleaned by backflow of liquid and calcinations. In this work we revealed laser treatment modes that can be used in order to form nanoporous structures in Cu-Zn system alloy.

2. The material under study and experimental equipment
Distinctive features of formation Cu-Zn alloy structures under the impact of high-intensity energy flows on its surface have been experimentally studied. As a model, was used a two-component Cu-Zn alloy “brass of 62%” with a 60.5…63.5 % content of copper (Cu), which feature is a significant concentration of the component (Zn) with higher vapor tension. During experimental studies, an important advantage of the said model material is that the reduction of Zn concentration in the surface layer can be visually observed, because the brass changes its color from the original yellow to red.

The energy deposition was effected by a gas CO2-laser ROFIN DC 010, with output power ranging from 100 to 1000 W and the output beam diameter of 20 mm. The original beam was transformed with a diffractive optical element (DOE) with the working surface shape of hyperbolic paraboloid. It performed the required focusing of laser light [5]. The temperature in the heating area was monitored using a non-contact pyrometer Kelvin - 1300 LZM with the temperature measurement range from 600 to 1600 K.

3. Results and discussion
We have realized the laser treatment modes that can be used in order to form nanoporous structures in Cu-Zn system alloy. The exposure to periodic laser pulses with the pulse-repetition rate up to 4000...5000 Hz – provided that the material is being heated below the melting point – makes it possible to produce a steady stress on the sample surface. It is suggested that a major mechanism behind the structure formation is the familiar mechanism of sublimation of the alloy component with higher vapor tension (Zn). A concentration gradient is formed within the material, leading to the sublimation of the said component from the surface according as it diffuses to the surface.

In the course of time, the thickness of the zinc diffusion layer increases, with the diffusion becoming a governing factor of the sublimation process. It is established that the laser treatment produces in the near-surface layer a cellular nanoporous structure with an average pore size of 40...50 nm. The nanopores are uniformly distributed within subgrains, being relatively stable in size and shape. Such a structure is formed owing to the formation of vacancies and their coagulation as a result of zinc sublimation from the material surface, development of a concentration gradient and the toward-surface diffusion of the material with a relatively high vapor tension.

The proposed patented [6, 7] technology is promising for manufacture of catalysts and ultrafiltration membranes.

4. Conclusion
Laser treatment modes have been identified making it possible to form nanoporous structures in metallic materials, during this process the material being heated below the melting point. Conditions of the formation of structures with nanopores ranging in size from 40 to 50 nm by laser exposure with the pulse-repetition rate up to 4000...5000 Hz in a model metallic material – a two-component alloy “brass of 62%” have been defined. After the laser exposure a structure with sufficiently uniform distribution of pores is formed on the sample surface within a exposed area. Such a structure is formed owing to the formation and coagulation of vacancies and caused by zinc sublimation from the material surface, creation of a concentration gradient and the toward-surface diffusion of the material with a relatively high vapor tension.
References


LASER-INDUCED CHEMICAL LIQUID-PHASE DEPOSITION OF COPPER ON TRANSPARENT SUBSTRATES

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Laser-induced chemical liquid-phase deposition allows maskless manufacturing of metallic structures on the surface of dielectrics and is prospected to be a promising tool in the field of microelectronics and microfluidics. In this work conductive copper lines were deposited at the backside of soda lime glass substrates by using a focused, scanning ns-pulsed Ytterbium fiber laser at 532nm wavelength. The deposition process is initiated by a photothermal reaction of a CuSO\(_4\)-based liquid precursor in contact with the backside of the substrate. Deposits were characterized by Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectrometry (EDX), Atomic Force Microscopy (AFM) and 4-point-resistivity-measurements. The obtained copper deposits are crystalline, stable under ambient conditions and have a conductivity in the same order of magnitude as bulk copper.

1. Introduction

An interesting application for laser surface processing is the fabrication of metallic micro-structures with high lateral resolution. Such structures can find application in many fields of technology, such as in microelectronics, optoelectronics, micromechanics especially for sensor and actuator devices. One way to deposit such structures is laser-induced chemical liquid-phase deposition (LCLD), a simple and cost-effective deposition method, where neither expensive vacuum exhaust and gas systems, nor spin-on, active site seeding or mask projection processes is required. In addition the components are rather cheap and easy to handle. LCLD is a well-known technique and is applied for a long time already [1-8]. In most of the LCLD setups the precursor liquid is placed on top of the substrate. In recent work, our group investigated an ablation technique called laser induced backside wet etching (LIBWE) [9, 10]. This technique allows smooth and controlled ablation of transparent materials using related setup components like LCLD and also related CuSO\(_4\)-based solutions as absorber liquids. Since in LIBWE the ablation is done at the back side of the substrate, it would be interesting to perform LCLD at the backside as well, regarding the promising possibility to combine these two processes, i.e. ablation and deposition. In this paper, copper structures fabricated at the backside of the substrate (i.e. with an “inverse” setup) are presented and discussed.

2. Experimental

The LCLD experiments were performed using a pulsed second harmonic Ytterbium fiber laser at 532nm wavelength and with a pulse duration of 1.4ns. (GLP-5, IPG Laser GmbH). The pulse repetition rate has been set to 300 kHz. A PTFE laser etch chamber with a reservoir for the CuSO\(_4\)-based liquid precursor of about 25ml and capable of fitting 50x50mm soda lime substrates was fixed on top of a height adjustable stage. The composition of the liquid precursor was: 0.1M CuSO\(_4\), 0.2M KNa-tartrate (Rochelle Salt, KNaC\(_4\)H\(_6\)O\(_6\) x 4H\(_2\)O), 0.125M NaOH and 6M formaldehyde (CH\(_2\)O). It was placed in contact with the downside of the transparent substrate. Laser light was irradiated from the front side of the substrate and was focused onto the solid-liquid interface region. A galvo-scanner with an f-theta-lens of 163mm focal length has been used to control the scanning pattern and the lateral velocity of the laser beam.

Figure 1: SEM-images of the initial baseline (overview on the left, detailed image on the right)
3. Results

3.1 Topography

It has been found that for the inverse setup used in our experiments, a two-step approach has to be applied. In a first step an initial “baseline” has to be performed, followed by superposed multiple line scans. For both steps satisfactory results could only be obtained with a defocused sample positioning. For the baseline a fluence of 55mJ/cm² per pulse, a scan velocity of 0.1mm/s and a focal plane in air 2.5mm above the liquid-sample interface have been used. This resulted in a roughened surface with adhering deposits formed with a random distribution of metallic islands (see Fig. 1). Using for the superposed multiple scans a fluence of 7mJ/cm² per pulse (a factor 8 less than for the baseline), a scan velocity of 2mm/s (a factor 20 higher than for the baseline), a focal plane in air 3.5mm above the liquid-sample interface and a number of sweeps between 800 and 1600, well defined, crystalline copper structures were formed over the whole roughened area (see Fig. 2). The defocusing as well as the reduced fluence for the multiple scans is necessary to avoid immediate laser ablation of deposited Cu-species.

3.2 Conductivity

Estimations about the cross-section of the deposited lines have been made by means of AFM-measurements. While the width of the lines was constant (approx. 55µm), the height and shape were dependent on the number of sweeps of the multiple scan lines, which lead to a cross-sections of ca. 6µm² to about 30µm². 4-Point-resistivity-measurements allowed calculating the specific conductivity of the deposited lines, taking in account the measured cross-sections for the corresponding lines. The found mean value of 1.4x10⁷ 1/(Ω*m) with a standard deviation of 0.3x10⁷ 1/(Ω*m) corresponds approximately to a quarter of the specific conductivity of bulk copper. This value remained stable even after storage of the samples under ambient conditions for weeks.

Further investigations will now examine the compatibility of the deposition process with antecedent LIBWE-microstructuring.

References

MAGNETIC PROPERTIES OF Zn\textsubscript{1-x}Co\textsubscript{x}O FILMS GROWN BY PULSED LASER DEPOSITION

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The work is devoted to the fabrication and studying the properties of the diluted magnetic semiconductor thin films of Zn\textsubscript{1-x}Co\textsubscript{x}O (x=0.05-0.45) grown on the c-sapphire substrates by the pulsed laser deposition method. It has been shown that the solubility limit of cobalt in the single-phase ternary solution of Zn\textsubscript{1-x}Co\textsubscript{x}O with wurtzite-type crystal structure produced in the low oxygen enriched ambient (~10\textsuperscript{-6} Torr) exceeds 35 at.%. The investigation of anomalous Hall resistance dependence on the magnetic field has revealed the presence of a preferential direction of magnetic anisotropy. The hysteresis dependence of transport and magnetic properties in the film samples of Zn\textsubscript{1-x}Co\textsubscript{x}O has been observed up to 130 K.

1. Introduction

One of the major directions of modern semiconductor spintronics is the search and investigation of the new magnetic semiconductor systems retaining spin polarization of the carriers at high temperatures. The recent theoretical estimates have shown that zinc oxide doped by transition (3d) metals can be ferromagnetic with Curie temperature higher than the room temperature, which makes this material a key one for semiconductor spintronics [1]. It has been experimentally established that of all 3d-metals cobalt has the highest solubility limit in the films of ternary solution Zn\textsubscript{1-x}Co\textsubscript{x}O produced by pulsed laser deposition [2]. The single-phase wurtzite films of Zn\textsubscript{1-x}Co\textsubscript{x}O with high structural perfection are paramagnetic [3] or even antiferromagnetic [4]. High-temperature ferromagnetism is observed only in the thin films of Zn\textsubscript{1-x}Co\textsubscript{x}O containing metallic nanoclusters of Co (or CoZn) [5]. Therefore, the prospects have currently been outlined for fabrication of ferromagnetic semiconductor nanostructures with high values of Curie temperature by the use of two-phase materials which can find application as spin injector into common semiconductors.

1.1 Experimental details

A series of Zn\textsubscript{1-x}Co\textsubscript{x}O films has been obtained on sapphire substrates of a c-cut by pulsed laser deposition. The ablation of the targets was carried out by the excimer KrF laser with pulse repetition rate of 10 Hz and energy density of 4.2 J/cm\textsuperscript{2} on the target. The quantity of laser pulses for each sample was exposed the same and made 2*10\textsuperscript{4}. The initial vacuum in the working chamber was ~10\textsuperscript{-7} Torr. The substrates were placed at a 70 mm distance from the target. The Zn\textsubscript{1-x}Co\textsubscript{x}O films were grown at the substrate temperature T\textsubscript{S}=500 °C. The synthesis of the films was performed in the range of buffer oxygen pressure from 4*10\textsuperscript{-6} Torr to 5 mTorr. The composite ceramic target of ZnO contained a sector of metallic Co.

1.2 Results and discussions

For characterization of the crystal structure and phase composition of the films the X-ray diffraction method was used. The X-ray scans of the Zn\textsubscript{1-x}Co\textsubscript{x}O films with cobalt concentrations of 25 at.% and 45 at.% are presented on Fig.1a. In the X-ray scan of the Zn\textsubscript{1-x}Co\textsubscript{x}O film with x=0.45 a diffraction peak was observed near 44.5°, corresponding to reflection from the plane (004) of the cubic phase of the Co\textsubscript{2}O\textsubscript{3} compound, or from the plane (400) of the cubic phase of the ZnCo\textsubscript{2}O\textsubscript{4} compound. Thus, the reached limit of cobalt solubility in the single-phase ternary solution Zn\textsubscript{1-x}Co\textsubscript{x}O with wurtzite crystal structure, produced in the low enriched oxygen ambient (~10\textsuperscript{-6} Torr), smaller then 45 at.%. The average size d of a crystal grain along the direction (00.1) increased from 0.32 nm to 22.5 nm at oxygen pressure buildup from 4*10\textsuperscript{-6} Torr to 5 mTorr. The characteristic variation dependence of Zn\textsubscript{1-x}Co\textsubscript{x}O film with x=0.25 on oxygen pressure in the vacuum chamber was studied. It was established that the average size d of a Zn\textsubscript{1-x}Co\textsubscript{x}O crystal grain along the direction (00.1) increased from 10 nm to 35 nm at oxygen pressure buildup from 4*10\textsuperscript{-6} Torr to 5 mTorr.

Hall measurements of the Zn\textsubscript{1-x}Co\textsubscript{x}O films have shown that they exhibit electronic conductivity. The research of transport properties of the Zn\textsubscript{1-x}Co\textsubscript{x}O films with Co content of 25 at.% has revealed that electron concentration n exponentially decreases from 1.2*10\textsuperscript{19} cm\textsuperscript{-3} to 5.9*10\textsuperscript{16} cm\textsuperscript{-3} with building up of oxygen pressure in the investigated range. It is obvious that so high electron concentration in the samples grown in the low enriched oxygen ambient is caused by high density of oxygen vacancies V\textsubscript{O}. The rise of oxygen pressure in the chamber leads to a significant decrease of V\textsubscript{O} density and to stoichiometric growth of the Zn\textsubscript{1-x}Co\textsubscript{x}O films. Thanks to growing of the average size d of Zn\textsubscript{1-x}Co\textsubscript{x}O crystal grain, the carrier mobility \( \mu \) in the films has increased from 0.32 cm\textsuperscript{2}/V*s to 22.5 cm\textsuperscript{2}/V*s in the range P from 4*10\textsuperscript{-6} Torr to 1*10\textsuperscript{-3} Torr.
The temperature dependences of transport properties of the Zn$_{1-x}$Co$_x$O films have shown that their resistance increases with temperature reduction. It is indicative of dielectric character of conductivity in the films. The investigation of magnetization, together with transport properties measurements, has revealed the presence of ferromagnetism in the samples of Zn$_{1-x}$Co$_x$O films with the cobalt content $x=0.25$, which were produced in the low enriched oxygen ambient. The field dependences of anomalous Hall resistance $R'_H$ and the magnetic moment $M$ for a sample of Zn$_{1-x}$Co$_x$O film ($x=0.25$), obtained at 5 K and 77 K, are presented on Fig.2. As seen from the figures, the hysteresis loop is observed in the field dependences of magnetization $M(B)$ and is missing in the transport measurements. This fact can be explained by different orientation of the film relative to the magnetic field. In magnetization measurements the magnetic field lies in the plane of the sample, while for Hall measurements the field is perpendicular to the plane of the film sample.

The investigations of transport properties of the Zn$_{1-x}$Co$_x$O films with the thickness $d=60$ nm suggest the hysteresis dependence of longitudinal resistance $R_{xx}$ on the field $B$ which has significantly grown in comparison with the samples of larger thickness. This observation can suggest the presence of directed magnetic anisotropy, or the existence of several phases with different coercive forces. It should be noted that the hysteresis dependence in the samples of Zn$_{1-x}$Co$_x$O films was observed up to 130 K.

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1.3 References
INFLUENCE OF BARRIER LAYER THICKNESS IN MODULATION-DOPED STRUCTURE Mg$_{0.18}$Zn$_{0.82}$O/$\delta$-Ni/$d$-Mg$_{0.18}$Zn$_{0.82}$O/ZnO ON TRANSPORT PROPERTIES

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The Mg$_{0.18}$Zn$_{0.82}$O/$\delta$-Ni/$d$-Mg$_{0.18}$Zn$_{0.82}$O/ZnO heterostructures with $\delta$-layer of Ni have been grown on c-sapphire substrates by the pulsed laser deposition method in the range of thickness $d$ from 0 nm to 15 nm. The influence of the temperature of thermal annealing of ZnO buffer layers on their morphology and structural properties has been investigated. It has been established that longitudinal resistance $R_{xx}$ of the structures under study nonmonotonously depends on the thickness of the Mg$_{0.18}$Zn$_{0.82}$O barrier layer with a minimum at $d=3$ nm.

1. Introduction

Spatial separation of charge carriers in conducting channels and ionized impurities in the barriers of modulate-doped structures allows significant increasing of carrier mobility. It is possible to increase the distance between mobile carriers and ionized impurities by introduction of undoped layers (spacers) into barriers. The transport properties of two-dimensional electronic gas have already been studied for application in high-electron mobility transistors based on MgZnO/ZnO heterostructures [1] and in quantum spin transport devices based on AlGaN/GaN heterostructures [2]. It was shown [3] that in GaAs-AlGaAs structures the carrier mobility monotonously increases as the thickness of undoped barrier layer varies from 0 nm to 15 nm. In this work we have studied the influence thickness $d$ of the Mg$_{0.18}$Zn$_{0.82}$O spacer on the transport properties of Mg$_{0.18}$Zn$_{0.82}$O/$\delta$-Ni/$d$-Mg$_{0.18}$Zn$_{0.82}$O/ZnO heterostructures containing Ni $\delta$-layer.

1.1 Experimental details

The series of samples of the Mg$_{0.18}$Zn$_{0.82}$O/$\delta$-Ni/$d$-Mg$_{0.18}$Zn$_{0.82}$O/ZnO heterostructures has been grown by pulsed laser deposition with different thickness of space layer $d$-Mg$_{0.18}$Zn$_{0.82}$O. The targets ablation was carried out by the excimer KrF laser with pulse repetition rate of 10 Hz and energy density of 4.2 J/cm$^2$ on a target. The initial vacuum in the working chamber was ~10$^{-7}$ Torr. The substrates were placed at a 70 mm distance from the target. The samples were grown at the substrate temperature $T_S=450$°C and the buffer oxygen pressure of 5 mTorr. The 300 nm thick buffer layer of ZnO was first grown on the sapphire substrate (00.1) and was annealed at high temperature.

1.2 Results and discussions

The investigation of surface morphology of the buffer ZnO layers by the atomic force microscopy method has shown that the surface roughness of as-grown films is about $R_z = 5$ nm. Such roughness of the buffer ZnO layer surface is caused by high density of dislocations due to a mismatch of lattice parameters in the plane of growth. To reduce $R_z$ and decrease dislocation density, the thin films of ZnO have been annealed in the oxygen atmosphere in the temperature range 700°-1100 °C. It has been established that the minimum surface roughness ($R_z = 1$ nm) is reached at the annealing temperature of 1000 °C [4]. Fig.1a represents the AFM-images of the ZnO films surfaces as grown and annealed at temperatures 1000 °C, and cross-sections to these surfaces. The structural properties of the films have been studied by the X-ray diffraction method. The full width at half maximum (FWHM) of X-ray reflection peak near of a lattice point (00.2) of the buffer layers makes $\Delta \Theta = 0.225^\circ$ (Fig.1a). High-temperature annealing of the buffer layers in the oxygen atmosphere leads to reduction of FWHM by an order of magnitude (up to $\Delta \Theta = 0.035^\circ$). The sharp reduction of surface roughness $R_z$ and FWHM of X-ray reflection peaks is due to decreasing of defect density and respectively, to an improvement in ZnO film crystallinity. Finally, the lattice mismatch between the buffer ZnO film and the barrier Mg$_{0.18}$Zn$_{0.82}$O layer did not exceed 0.66 % [5].

The Mg$_{0.18}$Zn$_{0.82}$O spacer layer of the thickness varying from 0 to 6 nm with a 1 nm step, and from 2 to 4 nm with a 0.5 nm step was grown on the annealed buffer ZnO layers. Then a thin Ni layer (1.6 nm) was deposited. After that the structure was covered by a cap Mg$_{0.18}$Zn$_{0.82}$O layer of 30 nm thickness. The structures were grown with the use of metallic masks in the Hall configuration. The bilayers Au (50 nm) / Ni (10 nm) were deposited as ohmic contacts. Fig.2a represents the image of the produced structures, and Fig.2b depicts the band gap diagram of the grown structures.
Fig. 1 The surface morphology (a) and X-ray Θ-2Θ scans (b) of the ZnO films as-grown and annealed at 1000 °C.

The longitudinal resistance $R_{xx}$ of the obtained $\text{Mg}_{0.18}\text{Zn}_{0.82}\text{O}/\delta-\text{Ni}/d-\text{Mg}_{0.18}\text{Zn}_{0.82}\text{O}/\text{ZnO}$ structures have been studied at room temperature. The dependence of resistance $R_{xx}$ on the thickness $d$ of $\text{Mg}_{0.18}\text{Zn}_{0.82}\text{O}$ spacer layers is illustrated on Fig. 2c. As seen from the figures, the $R_{xx}$ resistance of the structures exponentially decreases from 154.5 kΩ to 21.4 kΩ as the spacer layer thickness $d$ increases from 0 nm to 3 nm. It can be explained by reduction of scattering of two-dimensional charge carriers by the local electrical field which is induced by impurity ions of Ni δ-layer [6]. An exponential growth of $R_{xx}$ resistance was observed at further increasing ($d > 3$ nm) of the layer thickness. Such behavior is explained by the scattering at the heterobondary and by a reduction of carrier concentration at the interface with an increasing of the layer thickness $d$.

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1.4 References


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Laser microembossing is a mechanical driven non-thermal laser forming process which enables the direct fabrication of 3D microstructures in metal foils by replication. A simplified arrangement of laser microembossing is introduced which permits a more flexible and large-scale fabrication process. The capability of this new laser microembossing process was demonstrated by replication of the microstructures from moulds into thin copper foils using KrF laser pulses. The topography of the generated structures in the copper foil and the mould used were measured with scanning electron and atomic force microscopy. The fabricated micropattern in the copper foil shows a high accuracy regarding the spatial resolution and shape. Furthermore, a significant reduction of the surface roughness of the copper foil from 300 nm rms down to 7 nm rms was observed due to laser embossing.

1. Motivation

The development of new micromachining techniques are of great interest with regards to the ongoing miniaturization and the increasing complexity of microelectromechanical systems (MEMS). Standard techniques for 3D micromachining like (deep) reactive ion etching, crystallographic etching and LIGA (Lithographie (Lithography), Galvanoforming (Electroplating), Abformen (Moulding)) require complex and expensive manufacturing processes.

For polymers replication technologies are often utilized to enable mass production for acceptable costs due to the ability of material softening at low temperatures or the possibility of curing monomers to polymers. Microembossing is a promising replication technique which allows to overcoming limitations in the material and the surface shapes. However, currently microembossing is mostly used for polymers. To overcome this limitation the investigation of microembossing of metal sheets for forming 3D metallic structures attracts more and more attention. Laser microembossing is a mechanical driven non-thermal laser forming process. In the case of laser microembossing pulsed laser ablation of an auxiliary material or an absorbing coating which covers the workpiece provides the required energy for the embossing process. The fabrication of microstructures by laser embossing has been reported only in few studies [1-3]. One aim of this study is on one side to introduce a simplified arrangement and an improved methodology for the laser microembossing process which enables a more flexible and large-scale fabrication with an improved reliability. The second aim of the study is on the other hand the investigation of the efficiency of the arrangement by embossing microstructures in thin copper foils. The high quality of the laser microembossing process is shown by the examination of the generated microstructures by scanning electron microscopy (SEM), atomic force microscopy (AFM), and white light interferometer (WLI).

2. Experimental

In Figure 1 the scheme of the cross section of the experimental set-up is shown. The mould and the workpiece were placed onto a vacuum chuck. A polyimide foil (PI) was used to seal the whole vacuum chuck and acts simultaneously as laser beam absorber for the generation of the shock waves which enable the embossing process. The advantage of this set-up is that the work piece is not contaminated or affected by any kind of absorbing coating or debris from the laser ablation of the absorber. By simply taking away the PI-foil with all contaminations a clean formed work piece can be obtained. In contrast to common arrangements no transparent confining material [1] was used.

Figure 1: Schematic sketch of the experimental set-up.
The present experimental set-up without confining material enables (i) to use various laser sources also with short wavelengths, ultrashort pulse lengths, or extremely high power and (ii) allows to apply more than one laser pulse. The size of the area patterned by microembossing is naturally limited by the laser spot size. In order to show the opportunity of scaling up the microembossing process multipulse laser scanning processes were studied. A KrF excimer laser with a pulse length of \( t_p = 25 \text{ ns} \) and a wavelength of \( \lambda = 248 \text{ nm} \) was used. Further, 6 \( \mu \text{m} \) thick commercial copper foils were used as work piece. In order to enable systematic studies of the embossing process different moulds were used. The pattern sizes of the moulds were varied in a range from tens of \( \mu \text{m} \) to sub-micrometer.

3. Results and discussion

Selected microstructures which where generated in copper foils by laser embossing are shown in figure 2. These patterns were made by laser scanning and it is clearly shown that the embossed pattern size exceeds the beam size (100 \( \mu \text{m} \times 100 \text{ \( \mu \text{m} \)) by far and that no superstructure due to the laser scanning occurs.

![Figure 2: (left) SEM image of a copper foil after the laser embossing process, (right) optical microscope image of a copper foil which was face to face with a mould. In area (II) and (III) the copper foil was laser-embossed onto a mould. The lines in area (III) are laser-embossed microstructures of the corresponding replicated mould. The sample was not treated in area (I).](image)

It was noticeable that the pattern-free areas which are surrounding the laser-formed microstructures have a much higher reflectivity compared to the unaffected areas of the pristine sample. In figure 2 (left) an optical microscope image of a copper foil after the embossing process is shown. Apart from the formed line patterns in area (III) the morphology, the surface texture, and the microtopography are changed within the laser-irradiated areas (II) and (III) in comparison to the untreated surface of the copper foil in area (I). The surface roughness in area (II) is significant reduced compared to the untreated area (I). Especially the regular rolling structures and streaks which can be seen in area (I) completely disappear in area (II) due to the laser embossing of the flat, unstructured master surface. To study this effect more in detail this “smoothing” was quantified by WLI and AFM measurements in several regions of the areas (I) and (II). In the untreated area (I) the measured surface roughness by AFM (50 x 50 \( \mu \text{m}^2 \)) was in the range of \( \sim 300 \text{ nm rms} \). In the laser-embossed areas (II) and (III) the surface roughness was drastically reduced and an average surface roughness of \( \sim 7 \text{ nm rms} \) was measured. The surface roughness reduction can be explained by forming the smooth surface of the moulds into the initial rough metal foil. Therefore, the hardness, the stiffness, and the surface quality are important issues for the master for the smoothing effect of laser embossing.

References

Laser Induced Forward Transfer of SnO$_2$ for Sensor Applications

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Laser-Induced Forward Transfer (LIFT) is a deposition method utilizing a laser to transfer a thin layer from a target onto a receiver substrate with a lateral resolution in the micron range. In this work results on LIFT printing of SnO$_2$ onto gas sensors is presented. Different approaches for preparing LIFT donor substrate were tested. The films were prepared by spin coating commercially available SnO$_2$ nano-particles and tin based metal-complex precursors. The material was transferred onto sensor microstructures and tested for sensitivity towards ethanol.

1. Introduction

Highly sensitive and reliable gas sensors are widely used for detecting different gases for e.g. air quality monitoring and safety applications. Tin dioxide as a cheap and non-toxic material is often used in commercial gas sensors. SnO$_2$ is a n-type semiconductor which reversibly changes conductivity depending on surface composition and environment.[1] Different methods are used to coat commercial SnO$_2$ sensors like sputtering or ink jet printing. Selective coating of the sensing area is required in the production process.

LIFT is a solvent free process and capable to transfer different materials with a high lateral resolution.[2] Selective and solvent free printing onto e.g. single sensors would improve and simplify the production. LIFT as a printing technique was already used successfully in printing different active materials onto sensors.[3] In the following the authors present the results on SnO$_2$ printing onto miniaturized gas sensor.

2. Transfer conditions

Different donor substrates for SnO$_2$ transfer with and without triazene polymer (TP) as a dynamic release layer were prepared and transferred using a XeCl excimer laser ($\lambda$=308 nm). Besides using spin coated SnO$_2$ nano-particle films a new approach with transfers of films based on metal complex precursors was used. These metal complex precursors were prepared with SnCl$_2$(acac)$_2$. SnCl$_2$(acac)$_2$ can be decomposed by the laser and therefore a transfer without TP is possible. A subsequent heating step transforms the material to SnO$_2$.

In order to evaluate optimal film composition and transfer fluences the differently prepared donor films were transferred in fluences of 50 to 500 mJ/cm$^2$ using single or double light pulses (see fig 1).

Optimal transfers of the SnCl$_2$(acac)$_2$ films were achieved using no or 200 nm TP layer and a wide fluence range of ~300 ± 50 mJ/cm$^2$. Successful transfers are possible using single or double pulse. Films consisting of SnO$_2$ nano-particles transfer only in a narrow fluence range (50 mJ/cm$^2$) and by applying two consecutive pulses.

Figure 1: Images of transfers with one and two laser pulses in the energy range of 50 to 500 mJ/cm$^2$ of SnO$_2$ nano-particles and SnCl$_2$(acac)$_2$. For SnCl$_2$(acac)$_2$ successful transfers are possible within a wide energy range and for one and to pulses. Nano-particles can be only transferred with two pulses in a narrow energy window.
3. Sensor sensitivity

Transfers under optimal condition were carried out onto sensor microstructures. The conductivity in synthetic air and the sensitivity towards ethanol at elevated temperatures of about 400°C was measured. Different values for the conductivity and sensitivity were observed for the different preparation methods of the donor films. With all the described systems ethanol (10 ppm) in dry air (see fig 2) could be detected. SnCl₂(acac)₂ based sensor-films showed a lower initial resistance and better performance compared to sensor based on SnO₂ nano-particles.

![Figure 2: Resistance change with different ethanol concentration of SnO₂ transferred from SnCl₂(acac)₂ (no TP, single pulse).](image)

References

PULSE LASER DEPOSITION METHOD OF ALKALI HALIDES FOR UV-PHOTOCATHODE PRODUCTION

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Production method of alkali halides UV-photocathode’s durable to environment exposure was proposed. Photocathode’s with high homogeneous and adhesion photoemission layer were made. Quantum yield of manufactured photocathode’s measurements results are presented. The developed method is promising for creation high aperture electron injectors and detectors.

1. Introduction

UV-photocathode’s have wide application as UV-detectors, electron injectors for acceleration facilities and etc. Especially actual problem is creating wide aperture UV-photocathode’s with homogenous photoemission layer, which can withstand exposure to air without degradation of quantum yield. Pure metals have low quantum efficiency even after laser cleaning of emitting surface [1]. Common method to improve quantum efficiency is to cover metal surface by alkali halides. This method uses complex and expensive vacuum equipment, but still to get good homogenous film with good adhesion and quantum yield one should to have enormous experience in such technologies. In paper [2] pulse laser deposition (PLD) method was used to cover metal substrate by Mg thin film. Pure film with high homogeneity and adhesion was achieved. Known [3] that alkali halides films considerably improve quantum efficiency of pure metal. Also such coatings withstand exposure to air, that allows creating wide aperture UV-photocathode’s without requirement enormous high vacuum chamber and sophisticated soldering and welding techniques.

2. Production

PLD has long been known and used for various applications. This technique particularly effective for production films with complex stoichiometry, growth speed is high, mechanical parameters also very good. To implement the PLD film growth of halide compounds we have developed and manufactured vacuum chamber and pulsed solid state laser, with passive Q-switch (LiF). Laser parameters are: pulse duration – 100ns, wavelength – 1064nm, frequency < 20Hz, pulse energy < 1J, TEM00. Fig. 1 shows a schematic of the film growth principle.

![Figure 1. PLD process of UV-photocathode production.](image)

As substrate we used Cu and Ni flat disks with 1.5mm thickness and 20mm diameter. Our preliminary tests showed that quality of produced films greatly depend on target and substrate preparation. We had pure CsBr compound in powder form, so we press it into dense tablet, CsI compound was in crystal form so any additional preparation not required. Substrate preparation was: mechanical cleaning by fine grinding paper, laser cleaning, chemical cleaning in hydrochloric acid solution, washing in distilled water, drying at room temperature. After all preparations have been done, target and substrate are placed into vacuum chamber, foreline pump and turbomolecular pump produced vacuum about 10-5 torr and then pulsed laser was on. It’s important pulsed laser to work in threshold regime, then plasma plume exist, but not much power putted into each pulse. In other way film can be damaged by big fragments of target. The substrate and the target should be set to normal with respect to each other, incidence angle of laser radiation about 450 to normal of target. Film thickness is governed by the time the process, was controlled by interferometer, we got about 2 min to produce optimal 0.5um thickness [3]. When PLD process is over, substrate was annealed for 3 hours in 600C and then got out from vacuum chamber to environment.
3. Quantum yield measurements

After 10 minutes exposure to air, we mount photocathode and tungsten mesh (35µm diameter, 520µm step) into Teflon holder, distance from cathode to mesh was set to 2mm. Mesh was soldered to positive electrode of high voltage power source. Assembled unit was put into measurement vacuum chamber (10⁻⁷ torr). Fig. 2 shows circuit diagram of measuring setup. As UV sources we used ArF and KrF excimer lasers with wavelength 193 and 248nm respectively, pulse duration was 5ns, frequency - 100Hz, average power was less than 1mJ.

Figure 2. Quantum yield measurement circuit. A – anode mesh, K- photocathode, Ck=100pF – cable capacity, K1 – discharge switch, C=10nF – isolate capacity, R= 1MΩ – measurement resistor, Vb=0-20kV HV.

UV spot was 1-3mm diameter, regulated. Varying voltage applied between photocathode and mesh, we got response signal onto oscilloscope Tektronix TDS 2022B. Response signal was broadened because of RC constant of measuring circuit (about 100us in our case). We increase voltage until linear increase of response signal was broken. This point determined as saturation, i.e all incident UV light used to produce electrons. By measuring incident light energy and calculating electrical charge from area under the response signal curve (1) we got quantum yield (2).

\[
Q = \int_{-\infty}^{+\infty} I(t)dt = \int_{-\infty}^{+\infty} \frac{U(t)}{R} dt \quad (1),
\]

\[
Y = \frac{N_{el}}{N_{ph}} = \frac{Q}{W} \cdot \frac{\hbar \omega}{1} \quad (2),
\]

where Q – electrical charge, I(t) – current, U(t) – voltage, R – measuring resistance, Y – quantum yield, \( N_{el} \) – number of emitted electrons, \( N_{ph} \) – number of incident photons, W – UV light energy, \( \hbar \omega \) – single photon energy.

4. Results and discussions

Better result was obtained with Cu substrates, achived quantum yield presented in Tab 1. To compare PLD technique we manage production of CsI photocathode on Cu substrate by more traditional thermal evaporation technique. PLD shows worse maximum yield, but films were very homogenous and quantum yield in different spots of photoemission area did not differ more than 20%.

<table>
<thead>
<tr>
<th>Material</th>
<th>Quantum yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>CsI, PLD growth, ( \lambda=193)nm</td>
<td>1x10⁻²</td>
</tr>
<tr>
<td>CsI, thermal evaporation, ( \lambda=193)nm</td>
<td>1.5x10⁻²</td>
</tr>
<tr>
<td>CsBr, PLD growth, ( \lambda=193)nm</td>
<td>3.3x10⁻²</td>
</tr>
<tr>
<td>CsBr, PLD growth, ( \lambda=248)nm</td>
<td>1x10⁻⁴</td>
</tr>
</tbody>
</table>

Table 1. Quantum yield measurement results.

Vapor sample showed very poor homogeneity, yield even disappeared in some areas. Also vapor provide poor adhesion, photoemission film was went away by slight rubbing by finger, PLD samples show very good adhesion, film endure high pressure friction by rubber material. Achieved quantum yield results are much lower, known in literature [4]. We attribute this to the fact that the time spent in the air, the coating has absorbed more moisture, and annealing in the measurement vacuum chamber we have not performed.

References
PYROMETRIC MONITORING OF GAS-ASSISTED CUTTING OF STEEL USING FIBER LASER

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Measurements of the temperature in zone of action of laser radiation on the molten metal have been performed. The results are reported for different speed of cutting of mild-steel plate of 3 mm-thick with high-power fiber laser; oxygen was used as an assisted gas. Researches demonstrate that fluctuations of local temperature are related to unequal radiation absorption that associates with local deformations of surface of melt. Thus noise spectrum of those fluctuations reflects turbulent surface deformation caused by gas jet and capillary waves. The standard temperature deviation does not exceed 10 K on the frequency of 7 KHz and above, and power law of spectrum of density of fluctuations of local temperature is about $-2.8$ in range of capillary turbulence. Thus we can distinguish radiation pulsation due to laser cutting from other processes of radiation affection to the sample, including unwanted, degrading the quality of technological operations. The paper focuses on investigation of high frequency part of measured spectra, what is important to reduce the response time of emerging reaction on deviation from the given regime of laser cutting. The results of investigation can be useful for monitoring laser cutting process.

1. Introduction

Sheet-metal laser cutting is the largest, in terms of market of machinery, widespread industrial laser application. An investigation of the dynamics of the laser radiation action on the material and a development of the monitoring systems is one of the directions of quality improvement in laser-thermal technology. It can be mentioned a few papers published recently aimed to improve the performance of the cutting [1-5], all of them related to thermal technology using CO$_2$ laser. We investigated local thermal luminosity of melt in process of fiber-laser cutting of metal sheet using multichannel pyrometer, as described in [6]. The cutting with fiber laser is competitively solution since nearly 2006 [7], but researches on the characteristics of fiber-laser applications are still few in number.

2. Experimental setup and results

A series of experimental cutting of a low-carbon steel sheet of 3 mm thick was made using Ytterbium-doped fiber laser YLS-3000 [IPG Photonics] with oxygen as an assist gas. The cutting speed was varied from 30 to 60 mm/s in experiments on cutting different specimens; the recommended speed of cutting metal plate of 3 mm thick was 40 mm/s for laser power of 1800 Watts. The pressure of oxygen was (0.3…0.5) MPa. The local brightness temperature was measure from the different depths on the cutting front (0.6 mm, 1.2 mm, 1.8 mm and 2.4 mm).

A luminosity of local area, about $\varnothing 100 \mu m$, on the cut zone heated by laser radiation is collected by an optical lens and illuminates the end face of optical fiber located at an angle of $\sim 30^\circ$ to the plane of the sheet. The light delivered by each of four optical fibers to the own photo-sensor. The arrays of photo-sensors K1713-05 [Hamamatsu] are used. This type of detector incorporates an infrared transmitting Si photodiode mounted over an InGaAs PIN photodiode along the same optical axis. Thus the measurement of brightness temperature applied the two-color method of pyrometry: the local brightness temperature defined in this case as a function of ratio of photocurrents of two photodiodes sensitive to neighboring regions of the near infrared radiation spectrum. We used rejected filter to reduce the penetration of laser radiation to optical path of pyrometer. Some results are shown on fig.1-2.

![Figure 1](image1.png)

**Figure 1:** The oscillogram of temperature on depth of 0.6 mm (lower line), 1.8 mm and 2.4 mm (upper line) with cutting velocity 50 mm/s and pressure of oxygen is 0.4 MPa.

![Figure 2](image2.png)

**Figure 2:** The dependence of the averaged temperature at 2.4 mm on cutting velocity in the same conditions.
2.1 The noise-like spectrum of temperature fluctuations

The results of measurements of the temperature fluctuations allow to calculate noise spectra of the temperature pulsations for the above-mentioned condition. The measurements were obtained by multichannel pyrometer on the various depths that allows us to trace spectra transformation along the front of cutting along front of cutting. Averaging of power of spectra makes it possible to enhance the relative amplitude of resonance oscillations against the background of random oscillations. Some of that low-frequency resonance coupled with the roughness and longitudinal strips [8], but high-frequency resonances are additive interferences that must be borne in mind when analyzing the spectra. Standard deviation $\sqrt{E_r(\omega)}$ corresponding to variance spectrum of temperature is calculated as base to further investigations of physical factors affecting temperature variations in the zone of gas-assisted laser cutting of metals: spectra of pulsations of the local brightness temperature were obtained to define ranges of influence of different melt surface deformation mechanism and to define the parameters of capillary waves distribution.

2.2 The spectrum of density of turbulent-energy dissipation

The function $\varepsilon = E_r(\omega) - \omega^2$, having the meaning density of turbulent energy dissipation [9], was calculated. This function has the maximum in hydrodynamic turbulence on the boundary between inertial and viscosity domains and tends to zero in the high-frequency area. The measurements show the existence of conditions for developed turbulent flow in range (1…7) kHz. The maximum of $\varepsilon$ is different for cutting conditions: its value rises with increasing of cutting velocity and oxygen pressure in described range of parameters. The maximum of $\varepsilon$ is localized near depth of (1.2…1.5) mm along the cutting front.

2.3 The phenomenon of capillary-wave turbulence

Consider another auxiliary function $\Theta(k) = E_r(k) - k^2/\omega$, where $k$ is wave number, and dispersion $k^3 = \omega^2(\rho/\sigma)$ ($\rho$ is melt density, $\sigma$ is melt surface tension). Function $\Theta$ is near to constant in case of capillary–wave turbulence with low frequency energy input [10]. Capillary waves we obtained are intensified with cutting velocity increasing. The range of capillary-wave turbulence expands along the cutting front. The function $\Theta$ is near to constant for capillary-waves shorter than 0.45 mm. The maximum of energy of short capillary-waves is on depth of (1.2…1.5) mm.

3. Conclusion

These researches demonstrate that we can estimate the mechanism and regime of laser cutting by measuring the spectrum of heat emission pulsations. It is shown, that local fluctuations of $T$ are related to local melt’s surface deformations due to unequal radiation absorption. Thus noise spectrum of $T$ fluctuations reflects turbulent surface deformation, caused by gas jet and capillary waves. Furthermore, the paper focuses on investigation of high frequency part of pulsation spectra, what is important to reduce the response time of emerging reaction on deviation from the given regime of laser cutting [11]. So the results of investigation can be useful for development of monitoring and quality control system of laser cutting process.

4. Acknowledgement

The authors wish to thank the Russian Foundation for Basic Research for financial support (grant N 11-08-01094-a).

References


OBSERVATION OF THERMOCAPILLARY EFFECT IN GAS - ASSISTED CO₂ LASER CUTTING OF STEEL

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Investigations of melt’s dynamics have been performed with pyrometer in the gasjet-assisted CO₂ laser cutting. Pyrometer consists of 4 sensors and local luminosity of metal melt has been measured precisely on different depth along front of cutting with long dimension resolution about 0.1 mm and with time resolution as short as 0.06 ms. The results of data processing are reported for laser cutting of mild-steel plate 3 mm, 6 mm and 10 mm thick. Brightness temperature was obtained from each sensor as ratio of currents of Si photo-diode and InGaAs photo-diode illuminated by the same light that allows obtaining spectra of melt’s surface deformation for different values of cutting velocity and assisted gas pressure. The generation of capillary-wave turbulence following thermo-capillary effect can be observed in the locations, where intensity of radiation of CO₂ laser on melt’s surface exceeds 1 MW/cm². The R-M-S of temperature fluctuations is greater than 10 K in the range of sub-millimeter capillary waves. Thus, an additional mechanism of the anomalous absorption on the front of cutting can compensate the low absorption of the metal in case of 10.6 µm laser in comparison with the absorption of the metal in the near infrared range.

1. Introduction
An investigation of the dynamics of the laser radiation action on the material and a development of the monitoring systems is one of the directions of quality improvement in laser-thermal technology [1-4]. We have previously carried out the comparison studies on the pulsation spectrum of integrated luminosity of emission from the laser cutting zone [5], the spectrum of brightness temperature under two-color pyrometry [6], and the spectrum of the side edge roughness, resulting from laser cutting [7]. This paper reports the results of measuring by a four-channel two-color pyrometer of pulsations of local temperature in the region of exposure of mild-steel plate by radiation of CO₂ laser.

2. Experimental setup
The experiments were made used “Trumatic L2530” machine (Trumpf GmbH, Germany) with a CO₂ laser of 1500 W power. Cuts of a low-carbon steel sheet of 10 mm thick were made. The “optimal” cutting parameters were used with the lens of 127 mm focus. The cutting velocity was varied ±20 % from the recommended velocity being 20 mm/s. Oxygen was used as an assist gas, its pressure being varied in range of (0.03…0.08) MPa. Experimental cuts of 6 mm- or 3 mm- thickness sheets of low-carbon steel were made with “optimal” cutting parameters too. The cutting velocity was varied (26…40) mm/s for 6 mm steel plate. The pressure of oxygen was varied (0.1…0.45) MPa. The cutting velocity was varied (35…60) mm/s for 3 mm steel plate, and the pressure of oxygen was varied (0.1…0.25) MPa.

Measurements of time fluctuations of local luminance of metal melt were performed during cutting. Thus the brightness temperature T has been taken from small illuminated areas located on different depth on the front of cut:
- in the samples of 3 mm thick the depth was 0.6, 1.5 and 2.3 mm;
- in the samples of 6 mm thick the depth was 0.6, 1.5, 2.3 and 4 mm;
- in the samples of 10 mm thick the depth was 1.5, 2.3, 3.2 and 4.8 mm.

These data permitted to determine temporal spectra of pulsations of brightness temperature. The procedure of data processing has been described in [8]. The dependences of T averaged values and corresponding dependences of the root-mean-square oscillation of its amplitude on the velocity of beam motion were obtained at various depths along cutting front for cutting parameters mentioned above.

3. Results and discussion
The spectrum of variance of temperature pulsations we obtained can be divided into three regions. Each of them derived from the different physical process. The low-frequency region I (below 300…700 Hz) coupled with cutting velocity and with transverse striations on the side edge of the plate [2, 7]. Region II includes frequency of melt ejection f = ωm/h (ωm is melt velocity, h -sample thickness). The temperature pulsations associated here with more detail peculiarities of the melt flow. It includes, for instance, the longitudinal striation on the side edge [9]. One should note that the melt flow has complicated formation similar to a mountain stream. The spectrum of variance of temperature pulsations in range II is deformed with increasing pressure of assisted gas in experiments. We will take a special attention in this paper to region III, in which the pulsations originated from capillary-wave turbulence on melt’s surface [10].

3.1 The energy of melt’s surface deformation
It is shown early [8] that local fluctuations of T are related to local melt’s surface deformations due to unequal radiation absorption. Thus, variance spectrum of temperature fluctuations on local surface E(T)(ω) is related with spectrum of
density of energy of surface deformation, caused by forced turbulent pulsation of melt flow \( \text{(II)} \) and local non-uniformity of surface tension \( \text{(III)} \). The function \( \epsilon = E_p(\omega) - \omega^2 \), having the meaning the density of dissipation of turbulent energy of surface deformation, was calculated from experimental estimation of \( E_p(\omega) \). This function has the maximum in hydrodynamic turbulence on the boundary between inertial and viscosity domains and must tends to zero in high-frequency area. The measurements show the existence of conditions of developed turbulent flow in case of cutting samples of 3 mm and 6 mm thick, in contrast to the data measured during cutting samples with thickness of 10 mm.

3.2 The transmission of energy of capillary waves throughout turbulent spectrum

The measured estimation of spectrum \( \epsilon \) in some cases does not tend to zero in the area of viscosity dissipation of hydrodynamic turbulence. Thus the capillary –wave turbulence reveals itself. Let’s consider another auxiliary function \( \Psi(k) = E_p(k) \cdot k^{-1/4} \), where \( k \) is capillary –wave number with dispersion \( k^2 = \omega^2(\rho/\sigma) \) (\( \rho \) is melt density, \( \sigma \) is melt surface tension). Function \( \Psi \) would be constant in case of capillary –wave turbulence with so- called inverse cascade: energy of capillary waves is transferring from short-length wave up to long-length capillary waves due to decay instability \( \text{(10)} \).

3.3 Thermocapillary phenomenon

The spectra of \( \epsilon \) do not tend to zero in the area of viscosity dissipation of hydrodynamic turbulence in specific cases of cutting namely in case of present of focused radiation in local zone of measurements. Function \( \Psi \) has small value of the same units if it measured in unfocused zone where capillary –wave turbulence weakened. We suppose the thermocapillary phenomenon of abnormal absorption \( \text{(11)} \) occurs in zone of presence focused, intensity above 1 MW/cm\(^2\), 10.6 µm radiation. The main reason of thermo-capillary effect is presence of thermal dependence of surface tension as showed in \( \text{(12)} \). For mild steels: \( \partial \sigma/\partial T = -0.6 \text{mN/(m·K)} \), and estimation of Marangoni number is \( \text{Ma}=10 \). Thus, an additional mechanism of the anomalous absorption of radiation can compensate the low absorption of the metal in case of 10.6 µm laser in comparison with the absorption of the metal in the near infrared range.

4. Conclusion

These researches demonstrate that we can estimate the mechanism and regime of laser cutting by measuring the spectrum of heat-emission pulsations. Thus noise spectrum of \( T \) fluctuations reflects turbulent surface deformation, caused by gas jet and capillary waves. Furthermore, the paper focuses on investigation of high frequency part of pulsation spectra, what is important to increase the reaction velocity to emerging deviation from the given regime of laser cutting. So the results of investigation can be useful for development of monitoring and quality control system of laser cutting process.

5. Acknowledgement

The authors wish to thank the Russian Foundation for Basic Research for financial support (grant N 11-08-01094-a).

References

ELECTRICAL PROPERTIES OF ZnO:Al THIN FILMS FABRICATED BY PULSED LASER DEPOSITION METHOD

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The results of fabrication and investigation of ZnO:Al thin films have been reported.

1. Introduction.

Transparent conductive oxides are widely used in thin-film solar cells, organic solar cells, optoelectronic devices, light emitting diodes, sensors, etc. Tin-doped indium oxide (ITO) is among of the most applicable materials of this class. But high cost of this compound necessitates the research in the field of the creation and characterization of the materials for the substitution of ITO.

1.1 Experimental details.

This work reports the investigations of the aluminum doped zinc oxide (ZnO:Al) thin films fabricated by the pulsed lased deposition (PLD) method. The separation of droplets has been performed by the speed separation method. The experimental conditions (buffer gas pressure, substrate temperature, concentration of Al in the target, energy density) have been changed.

1.2 Results and discussions.

The dependence of the electrical and optical properties of the ZnO:Al thin films grown on the experimental conditions (buffer gas pressure, substrate temperature, concentration of Al in the target, energy density) has been determined. The optimum conditions of the ZnO:Al thin films deposition have been defined. The lowest value of resistivity ($4 \times 10^{-4}$ Ohm cm) in the ZnO:Al thin films has been found at 3 at% Al. The films with high transparency in the visible region (>90%) have been fabricated. The resistivity measurements of the ZnO:Al thin films with different carrier concentrations ($n_e$) have been carried out in the wide temperature range of 10 to 330 K. It has been demonstrated that the metal-semiconductor transition in the ZnO:Al thin films grown by the PLD method takes place at $n_e \geq 6 \times 10^{19}$ cm$^{-3}$.

So the experiments conducted let us govern the electrical properties of the ZnO:Al thin films in the wide range and change the conductivity character (metal or semiconductor behavior).

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High-conductivity transparent in the visible range SnO$_2$:Sb thin films (100 nm thickness) have been produced by the pulsed laser deposition (PLD) method on quartz substrates without a post-deposition annealing. The structural, electrical, and optical properties of these films have been investigated as a function of doping level, substrate temperature, and oxygen partial pressure during deposition. The SnO$_2$:Sb thin films have been grown at the substrate temperatures in the range from 25 °C to 600 °C and the oxygen pressures in the range from 10 mTorr to 100 mTorr. The minimum resistivity of the SnO$_2$:Sb films has been 1.2 $\cdot$ 10$^{-3}$ Ohm$\cdot$cm. The average transmittance of the SnO$_2$:Sb films has been 85 % in the visible range.

1. Introduction

Films of transparent conducting oxide (TCO) widely are used as transparent high-conductivity thin-films materials for application in different regions, such as solar cells [1], gas sensors [2], optoelectronic devices, high-temperature mirrors and flat-panel displays. Indium tin oxide (ITO) films usually are used for these applications owing to their unique optical and electrical properties [3]. However, the important deficiency of the ITO films applications is their high cost and the high temperature of growth that makes difficult their deposition on the flexible polymer substrates [4].

Alternative for the ITO films is the SnO$_2$:Sb (ATO) films for which there is a perspective of the temperature deposition and the high temperature of growth that makes difficult their deposition on the flexible polymer substrates [4].

1.1 Experimental details

A series of SnO$_2$:Sb thin films has been obtained on quartz substrates by pulsed laser deposition at the different levels of the antimony doping from 0 at. % to 8 at. %. The ablation of the targets was carried out by the excimer KrF laser ($\lambda$ = 248 nm) with pulse repetition rate of 10 Hz. The energy density was changed from 2 J/cm$^2$ to 4 J/cm$^2$ on the target. The initial vacuum in the working chamber was $\sim$10$^{-7}$ Torr. The SnO$_2$:Sb films were grown at the substrate temperature in the range from 25 °C to 600 °C and the buffer oxygen pressure in the range from 10 mTorr to 100 mTorr. The substrates were carefully cleaned in an ultrasonic cleaner for 25 min with acetone.

1.2 Results and discussions

In order to minimize the electrical resistivity of SnO$_2$:Sb films there is a need to optimize the doping level of the films and also the PLD parameters, such as the substrate temperature and the oxygen partial pressure during deposition. Figure 1 shows the variation of the electrical resistivity as a function of the antimony concentration in the SnO$_2$:Sb films ($\rho$) and the substrate temperature during deposition of the films ($Ts$). The dependence on the figure 1 ($a$) is presented for the SnO$_2$:Sb films which were grown at the substrate temperature of 300 °C and the oxygen pressure of 20 mTorr. The dependence on the figure 1 ($b$) is presented for the SnO$_2$:Sb films which were grown at the oxygen pressure of 20 mTorr from the target with the antimony concentration of 2 at. %. The film thickness was 100 nm.

It is observed from figure 1 ($a$) that the resistivity initially decreases with increasing of the antimony concentration in the SnO$_2$:Sb film, reaches a minimum at 2 at. % of antimony ($\rho \sim 1.2 \cdot 10^{-3}$ Ohm$\cdot$cm), and increases with further increasing of the antimony concentration in the film. The initial decrease in the resistivity is due to an increase in free carrier concentrations as a result of the donor electrons from the antimony dopant. This initial increase in carrier density in the SnO$_2$:Sb films was due to the substitutional incorporation of Sb$^{5+}$ ions at Sn$^{4+}$ cation sites or incorporation of Sb ions in interstitial positions. However, the resistivity, after reaching a minimum (at 2 at. %), increases with further increase of antimony concentration in the SnO$_2$:Sb film up to 8 at. %. The excess antimony doping introduces Sb$^{5+}$ ions, which act like acceptors that compensate for the donor levels created by the Sb$^{5+}$ ions [7]. Thus, the excess antimony doping decreases the carrier concentration in the film and consequently increases the resistivity. A dependence of the film resistivity on the substrate temperature ($Ts$) during deposition of the films is shown in the figure 1 ($b$). The resistivity gradually decreases with an increase in $Ts$ from 25 °C to 300 °C, and then remains almost constant up to 600 °C. The initial decrease in the resistivity with an increase in $Ts$ can be explained by the observed improvement in film crystallinity. XRD analysis indicated that the films grown at low temperatures (25-200 °C) were amorphous, while films grown at the higher temperatures (> 300 °C) showed a crystalline structure.
The optical transmittance spectra of the SnO$_2$:Sb films produced at the established optimal PLD conditions and the antimony concentrations were informed that the films had a high transparent in the visible range from 400 nm to 700 nm. The average transmittance of the SnO$_2$:Sb film was observed to be 85 % (figure 1 c). It was conditioned the effect of antireflection coating at the film thickness like $\frac{1}{4}$ of the light wavelength.

In conclusion, the production optimal conditions of the transparent high-conductivity SnO$_2$:Sb films have been determined by the PLD method. It was established the minimum resistivity of the SnO$_2$:Sb films ($\rho \sim 1.2 \times 10^{-3}$ Ohm·cm) have been observed at the substrate temperature of 300 °C, the oxygen pressure of 20 mTorr from the target with the antimony concentration of 2 at. %.

This work has been supported by grants RFBR № 11-07-12050_ofi_m_2011, 11-02-12200_ofi_m_2011, 11-07-00359_а, 11-02-92478_MNTI_а, 12-07-00301_а, 12-08-00642_а.

1.3 References

PRODUCTS ANALYSIS OF METALS LASER OXIDATION BY CHEMICAL THERMODYNAMIC METHOD

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Computational method for chemical analysis of products received by laser oxidation of stainless steel surface in atmosphere was described. It was shown oxides formation were the most probably. It was confirmed by energy-dispersive X-ray spectroscopy results.

1. Introduction
It is known, during laser irradiation color interference films form on stainless steel surface (and also for other metals and its alloys) due to chemical interaction with air [1]. On basis of this effect color laser marking technology is being developed. This technology implementation into the industry is prevented by difficulty of colors reproduction during the variation of processing material. To find a solution of interference colors “laser control”, which also allow to control surface optical properties, detailed information about physic-chemical processes taking place on metal alloys surface under laser irradiation is necessary, including chemical analysis of received films composition, conditions and kinetics of its formation etc [2].

Experimental methods of received films product analysis, such as Raman spectroscopy, energy-dispersive X-ray spectroscopy and other, are extremely labor-intensive (sometimes impossible) due to complexity composition for majority of alloys, for example stainless steel.

State of the art of chemical thermodynamic method with taking into account kinetic limitation allows getting computational solution for variety technological problems, particularly for estimation of received chemical compounds composition under laser irradiation. Suggested computational method allows to simplify estimation task of analysis received chemical compounds considerably.

2. The purpose of this work
The purpose of this work is chemical analysis of color films received during stainless steel surface laser oxidation in air by thermodynamic method of investigation (with taking into account kinetic limitation) and comparison of obtained results with date of chemical compounds by experimental (measurement) methods.

During laser irradiation of stainless steel type 12X18H10T surface in atmosphere (during the process of color image formation) various reactions of iron, nickel and chromium with oxygen, nitrogen, carbon and water are possible Depending on composition, temperature conditions of steel laser treatment and atmospheric composition the main physic-chemical processes and compounds of acquired interaction products are revealed by thermodynamic method (i.e. Gibbs free energy computation) and specifically developed model-calculation system with the assistance of relevant thermodynamic information (every compounds enthalpy and entropy for given chemical reactions)

Analysis of kinetic data available in literature (i.e. activation energy and Arrhenius coefficient for every chemical reaction) allows one to estimate kinetic limitation reaction of being studied and to reveal compounds the most intent to formation for diffusion and kinetic regimes.

Stainless steel samples composition with different color palettes (obtained during laser irradiation) was investigated by energy-dispersive X-ray spectroscopy. It made possible a comparison of experimental data with computational results.

4. Summary
In this paper chemical composition of films obtained during laser irradiation of stainless steel surface in atmosphere is revealed by chemical thermodynamic methods with taking into account kinetic limitation. It was shown that oxides formation is the most probably which are confirmed by energy-dispersive X-ray spectroscopy results.

References
LASER STRUCTURING OF GLASS-CARBON FOR IMPROVEMENT OF ITS EMITTING PROPERTIES

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Complex of laser micromachining operations for glass-carbon plate processing is described. The operations of laser scribing, milling, cleaning and marking were used for production of the cathode workpiece. The operation of structuring was applied for production of nanopeaks on the surface of the cathode beams. The nanopeaks self-organized in the process of the structuring. As a result we obtained a field-emission cathode with high density of current emission and a shorter technological route of its production.

1. Introduction

The production and study of emitting structures is an important problem in many scientific centers. The main purpose of these researches is enhancing field-emission cathodes manufacturing. It was found out that a very perspective substance for manufacturing of such devices is a graphite with its modifications, in particular, glass-carbon. This material has a valuable property to self-organize nanostructures on its surface under laser action. These structures provide high density of the emissive current from the cathode. Such cathodes can be applied in all electrovacuum devices with the high density of electronic streams and a microsecond available time.

2. Laser operations

The process is starting from a glass-carbon plate scribing with the Nd:YAG-laser. Laser scribing, milling, cleaning and structuring are applied for production of micropits on the surface of glass-carbon cathodes with high density of current emission.

Scribing of a 2 mm monolithic glass-carbon plate allows breaking a carbon preform. Laser milling is applied both for cutting of the cathode itself and for formation of the cathode beams. Cleaning of the cathode surface after laser milling (soot sedimentations removal) is carried out on the same equipment with changing mode. Laser structuring of the surface of each cathode beam is carried out by laser micrograving. In the process of micrograving the self-organizing of nanopeaks happens.

The elemental composition of glass-carbon plates is controlled by LIBS-method. The comparison of the preliminary prepared plate for traditional chemical cathode technique to the plate for laser technique showed that the plate for laser processing is much cleaner and has no surface deposits.

The produced structure represents a field of micropits of the dome-shaped form (Fig. 1) with the sizes of the basis of one peakt 10×10 µm and from 15 µm height. On the top of micropits chaotically located groups of nanopoints are formed, improving emitting ability of structure and the cathode as a whole. The structure provides the average density of the current 1 A/cm².

3. Acknowledgments

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GENERATION OF LASER INDUCED PERIODIC SURFACE STRUCTURES BY INDIRECT FEMTOSECOND LASER IRRADIATION

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Femtosecond (fs) laser structuring permits to obtain 3D nano-scale accuracy in surface modification with reduced distortion of the bulk material thanks to its damage-free material processing capabilities. Here we report about the generation of Laser Induced Periodic Surface Structures (LIPSS) on β-SiC irradiated by laser induced plasma produced by 40 fs laser pulses focused onto a Low Density Polyethylene (LDPE) foil. A Ti:Sapphire (wavelength 800 nm, electric field polarization perpendicular to the laser pulse direction) laser was focused on a 15 µm thick LDPE film facing a 130 nm thick β-SiC film. Regardless of the number of laser pulse applied, LIPSS are visible on all the irradiated areas with an average regular periodicity of 710 nm. We attribute the formation of LIPSS to the efficient coupling of the unfocused fs laser pulse to the incoherent extreme ultraviolet (XUV) component of the laser-produced LDPE plasma.

1. Introduction

The generation of LIPSS from fs pulse direct irradiation has been extensively investigated on various materials but the reported models do not appear sufficient to clarify recent observations during LIPSS generation in the fs regime of interaction [1, 2]. Thus, the complete process of LIPSS generation is still under discussion. A significant increase of both the frequency of occurrence and the peak-to-valley depth of LIPSS was recently observed with a complex experimental setup, when fs near infrared (NIR) laser pulses were applied to β-C together with a weak XUV beam with respect to NIR irradiation alone [3]. LIPSS enhancement was attributed to the combined XUV-NIR dual action. Here we show for the first time that LIPSS can be generated upon irradiation of β-SiC surface by low density polyethylene (LDPE) plasma produced by 40 fs laser pulses.

2. Experimental Setup

A β-SiC film, around 130 nm thick, was pulsed laser deposited on a Si (100) substrate kept at 1173 K using a Kr excimer laser (wavelength 248 nm, pulse duration 25 ns, fluence 6 J cm⁻²) at high temperature. A homogeneous, compact film, free from surface particulate was obtained. A Ti:Sapphire laser (wavelength 800 nm, pulse width 40 fs) was focused on a 15 µm thick LDPE film, directly facing the β-SiC film at the distance of 1 cm. Each laser pulse, with intensity on the order of 10¹⁸ W cm⁻², impinged on the LDPE inclined at 10° with respect to the normal to the surface. The laser-irradiated LDPE was converted to a highly energetic plasma carrying energetic C and H ions, which expanded and irradiated the β-SiC film.

3. Results and discussion

Different areas of the β-SiC sample were irradiated by LDPE plasma with different number of pulses, from 1 to 5, in order to observe the effects of progressively increasing cumulative pulse energy on SiC. Every irradiation produced on the sample a circumference with 4 mm diameter. All irradiated areas were analyzed by scanning electron microscope (SEM Zeiss Supra 40 field ion instrument). Independently of the number of laser pulses, a wavy surface morphology is present in all areas as shown in Fig. 1. Such a plasma-induced wavy morphology is clearly visible in the area irradiated by single laser pulse generated plasma and loses definition with increasing the pulse number. The wavy structure arises on the entire areas irradiated by the LDPE-originated plasma, without being limited to the center of a laser spot: indeed no laser spots are produced on the β-SiC surface, due to the indirect irradiation conditions. All irradiated areas were analyzed by atomic force microscope (AFM Bruker Dimension Icon with ScanAsyst and AFM Integra Prima, both working in tapping mode in air). Representative profiles of the irradiated areas are presented in Fig. 2a. Independently on the number of laser pulses, AFM profiles show that the wavy structure is characterized by a periodicity ranging from 638 nm to 826 nm with an average value of 710 nm, slightly smaller than the laser wavelength, and by a peak-to-valley depth ranging from 70 nm to 219 nm, leading to an average value of 123 nm.
Every area related to a definite number of pulses presents a specific, constant value of peak-to-valley depth and constant periodicity. The trends of peak-to-valley depth and periodicity with respect to the number of pulses (Fig. 2b) reveal a correspondence between the peak-to-valley depth and the periodicity when the number of pulses is kept fixed: a smaller peak-to-valley depth corresponds to a smaller periodicity.

The experimental results can be explained in terms of a simplified physical picture. The strong coupling between the NIR laser beam and the XUV/NIR-irradiated solid is attributed to efficient free electron generation via linear absorption of highly energetic XUV photons. Such clouds of free electrons undergo free-carrier absorption of NIR light, in turn leading to an increase in the absorption coefficient of optical radiation and consequently to a fast increase both of temperature and pressure in the near-surface region of the illuminated material. The resulting highly unstable state relaxes via material melting: the formation of rippled structures makes therefore possible an efficient relaxation of local tension at the material surface. On the basis of these results, the formation of the plasma induced ripples can be associated to the coupling of the unfocused fs laser beam to the incoherent XUV component of the laser-produced LDPE plasma. It’s remarkable that the incoherent XUV radiation is now obtained directly from the plasma, removing the need of HHG sources, and the NIR beam is out from the focus position.

4. Conclusion

In conclusion, we have shown that indirect fs irradiation of β-SiC with LDPE plasma brings to efficient LIPSS generation on the sample surface: these microstructures arise on the entire area irradiated by the LDPE-originated plasma, regardless the laser beam direction. Independently on the number of laser pulses, the observed morphology is characterized by an average regular periodicity of 710 nm, slightly smaller than the laser wavelength and it is most evident in the area that underwent a single laser pulse, losing definition with increasing pulse number. We attribute the generation of LIPSS to the effect of dual action of the unfocused fs laser beam with the incoherent XUV component of the laser-produced LDPE plasma. This is the first demonstration of LIPSS generation in a material being subjected to high intensity indirect fs laser irradiation.

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References:

In this paper, we use the methods of mathematical modeling to investigate the action on the silicon target of the pulse (picosecond) of laser with a wave length of $\mu = 0.5 \mu m$ and the photon energy exceeding the band gap of silicon $\hbar \omega > E_g$. The main feature of these modes is the impact of strong non-equilibrium processes of heating and melting, which is manifested in a large temperature difference between the carriers and the lattice.

Pulsed laser radiation is a widely used tool for precision machining of materials, including semiconductors. Among semiconductor materials, silicon was most widespread in the instrument-making and is one of the most promising materials for thin-film nanotechnology.

To optimize existing and develop new technologies of laser surface treatment of semiconductors it is necessary to perform a detailed study of the dynamics of processes occurring in the irradiation zone and leading to surface modification, including an analysis of the processes of heating, melting and evaporation.

In this paper, we use the methods of mathematical modeling to investigate the action on the silicon target of the pulse (picosecond) of laser with a wave length of $\mu = 0.5 \mu m$ and the photon energy exceeding the band gap of silicon $\hbar \omega > E_g$. The main feature of these modes is the impact of strong non-equilibrium processes of heating and melting, which is manifested in a large temperature difference between the carriers and the lattice.

The mathematical model consists of transport equations of the laser radiation, which takes into account the temperature dependence of the reflectivity of the surface, the carrier balance equation that takes into account generation (photo-ionization) and recombination of charged particles (Auger recombination, and photorecombination), the balance equations of energy carriers and the lattice, taking into account the absorption of laser energy, the exchange of energy between the electron and phonon subsystems, heat and mass transfer.

The basis of phase transitions of the 1st kind is the mechanism of heterogeneous melting and evaporation. The process of melting - crystallization is described in the approximation of the classical variant of the Stefan problem, evaporation - the approximation of the Knudsen layer (single-phase version of the Stefan problem).

Application of the method of dynamic adaptation to the numerical solution of differential equations in partial derivatives allowed determining the spatial and temporal distribution of temperature fields, explicitly distinguishing the position of the moving phase boundary, the speed of their movement, the lifetime of the melt and the thickness of the layers of melted and vaporized.

Typical time profiles of the laser radiation, temperature, media and lattice melting front velocity are shown in Fig. 1-3.
Figure 2. Time dependence of the melting velocity.

References


KINETICS OF PHASE TRANSFORMATIONS IN METALS UNDER ACTION OF ULTRA-SHORT HIGH-POWER LASER PULSES.”

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The methods of mathematical modeling were used to investigate the regimes of pico- and femtosecond action on metals - Al, Cu. The kinetics and dynamics of phase transformations are analyzed. The results of the modeling confirmed the skewness of the high-speed processes of melting – solidification. In particular, the maximum velocity of melting reaches the value of several kilometers per second, while the maximum velocity of solidification does not exceed hundred of meters per second. The temperature dependence \( \nu_{st} (T_{st}) \) does not have a sharp bend in the point of change of the direction of the phase transition.

The detailed analysis of the physical processes of the non-equilibrium heating and the fast phase transformations in the metal systems under the action of ultra-short laser pulses was performed in this paper. A mathematical model was built based on the brief analysis of the thermodynamical and kinetic approaches for the description of the phase transformations of the first order. This model is a non-equilibrium hydrodynamic version of the Stefan problem and describes the kinetics of high-speed heterogeneous phase transformations: melting, crystallization, evaporation. The model is supplemented by the explicit description of the moving phase fronts for correct reflection of the dynamics of the phase transitions.

The methods of mathematical modeling were used to investigate the regimes of pico- and femtosecond action on metals - Al, Cu. The kinetics and dynamics of phase transformations are analyzed. The results of the modeling confirmed the skewness of the high-speed processes of melting – solidification. In particular, the maximum velocity of melting reaches the value of several kilometers per second, while the maximum velocity of solidification does not exceed hundred of meters per second. The temperature dependence \( \nu_{st} (T_{st}) \) does not have a sharp bend in the point of change of the direction of the phase transition.

The deviation from the local thermodynamical equilibrium is noticed both in the bulk and at the interphase boundary. The response function \( T_{st} (\nu_{st}) \) has a linearly increasing character for low values of velocity \( \nu_{st} \) in the range of \( [0 \pm 50] \text{ m/s} \), Fig.1. As the velocity \( \nu_{st} \) rises more than \( \nu_{st} > 100 \text{ m/s} \), a maximum is formed in the response function for both metals. The appearance of the maximum means that the dominating mechanism of the phase transition changes: the mechanism of heat conductivity is changed by the hydrodynamic one. The maximum value of overheating of the interphase boundary reaches the value of 200 – 400 K, the one for overcooling is by one order lower than that value. The overheating and overcooling of the bulk are significantly higher - \( 4 \cdot 10^5 \pm 5 \cdot 10^3 \text{ K} \) for overheating and \( 6 \cdot 10^2 + 8 \cdot 10^2 \text{ K} \) for overcooling, Fig.2. The results for different materials are compared between each other and with experimental data.
Fig. 1. Response function for melting of Al.

Fig. 2. Spatial distribution of temperature in Al.
INVESTIGATION OF THE POSSIBILITY OF STRUCTURAL MODELING OF ELECTRON PROCESSES IN SEMICONDUCTORS UNDER FEMTOSECON LASER ACTION

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A simple experimental approach is proposed for correction and adjustment a mathematical model, which describes internal and external photo-effects in silicon under action of a femtosecond laser pulse. Basing on the polariton mechanism of surface microstructuring the approach implies comparison of experimentally observed microstructuring of semiconductor surface under ultrashort laser pulse with the experimental data on surface plasmon resonance at a model objects with similar optical structure under continuous excitation. The contribution of electron emission is evaluated depending on the femtosecond laser pulse duration.

Extensive theoretical studies, which are being currently conducted in interaction of ultrashort laser pulses with solids relay on experimental data for validation. The currently used experimental approaches such as femtosecond pump-probe technology and mass-spectroscopy provide measurement of integral characteristics, but have limited capability for retrieval of dynamics of the processes. Knowing the dynamics is critical for analysis of a complex non-linear process. The limitations of the experiment approach are being compensated by extensive use of mathematical modeling. Efficiency of mathematical simulation of the fast non-linear processes in a wide range of the initial data essentially results from alignment the model with the experimental data.

The two temperature model is the most widely used approach to description of non-equilibrium heating of a solid medium by ultrashort laser pulses [1]. Having been initially proposed for metals, this model has evolved to provide more precise description and include the processes, which accompany the heating. Practical application of the model is determined by correct estimation of optical and thermo-physical characteristics in a wide range of the temperature, and quantitative estimates for electron-electron and electron-photon interaction for description of electron gas temperature and energy exchange between the electrons and the lattice.

For femtosecond pulses the effects, which are related to hot electron emission, have to be taken into consideration [2-3]. For example, in metals external electron emission may facilitate a new mechanism of femtosecond ablation related to Coulomb explosion. In semiconductors the role of emission processes may be even more essential due to extreme increase in electron concentration over its initial magnitude due to action of a femtosecond laser pulse.

We propose a simple experimental approach to correction and adjustment of such a mathematical model without using expensive equipment. This approach is based on comparative analysis of surface plasmon excitations induced by an ultrashort laser pulse and those excited in stationary conditions.

According to the proposed approach we calculated a short-lived optical structure induced by the ultrashort laser pulse, and then reproduce it in a thin film multilayer sample. The sample is studied in stationary conditions by surface plasmon resonance technique. Comparison of the experimental study and the calculation results allowed us to adjust the major parameters of the mathematical model. We also determined the critical pulse durations in the femtosecond range, which determine whether emission flows have to be taken into consideration or they can be neglected to simplify the model.

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References
HIGH TEMPORAL RESOLUTION INVESTIGATION OF GRAPHITIC NANOSTRUCTURES FORMATION IN THE FIELD OF MILLISECOND PULSES OF GLASS: Yb, Er LASER RADIATION

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Abstract. In this work graphitic nanostructures were obtained with ablation on air of graphite rod under Glass: Yb, Er laser radiation with wavelength 1.54 µm and millisecond duration of pulses. In order to investigate main steps of graphitic nanostructures formation the process of ablation was recorded with high speed camera “FASTCAM SA4”. Characterizations of ablation plume such as angle of distribution and particles velocity were carried out with high temporal resolution.

1. Introduction
Different forms of graphitic materials are already widely used in science and technics. Recently, nanostructures with graphite-like atomic structure are objects of great interest. Such materials are presented with fullerenes, carbon nanotubes and nanoonions [1]. Structural characterizations of nanographitic materials lead to appearance of its unique physics, mechanical, optical properties, which could be useful in different scientific and industrial areas [2]. At present time there are a lot of works devoted to graphitic nanostructures preparation methods. Among them few different perspective methods should be noticed: thermal graphite evaporation, contact arc discharge, burning and pyrolysis of carbon contained substances such as naphthalene [3]. However these methods are very difficult in realization and require significant energy expenses, also they are distinguished with big impurity amount, because of electrodes dust exiting in the case of overheating, and ash formation during carbon contained substances burning. We can avoid such disadvantages of methods noticed above in the case of graphite laser ablation.

In this work carbon nanoparticles, first obtained at [4] with laser ablation on air of graphite rod, formation process would be shown by mean of high temporal resolution video recording of ablation plume.

2. Material and method
In this work radiation beam of Glass: Yb, Er laser with wavelength 1.54 µm and pulse duration 30±1 ms was focused on graphite rod (30% of graphite and 70% of inorganic filler consisted primarily of SiO₂, Al₂O₃ and H₂O) with round spot diameter about 1 mm. Products formed at the result of laser graphite ablation on air were collected on substrate surface (Fig. 1).

![Figure 1: Experimental setup. View of ablation plume at different time relatively to laser beam impaction of graphite rod: a) 3 ms; b) 15 ms; c) 30 ms](image)

This substrate was explored with optical and scanning electron microscopy methods. Sizes and forms of collected structures were estimated. Raman spectra were obtained using a laser Raman spectrophotometer InVia (Renishaw).

3. Results and discussion
It was found at the result of scanning electron microscopy (SEM) investigation of obtained structures that it consists of round particles with sizes varied from 20 to 100 nm. Such structures are assembled with each other and presented as porous nanofilm (Fig. 2a). Raman spectrometry showed a strong peak at 1578 cm⁻¹ and less one at 1350 cm⁻¹ (Fig. 2b), which are related to graphitic materials [5].
Intensive ablation plume formation was an evidence of graphite rod destruction. It was found that this process can be divided on three steps relatively to laser pulse impact moment: interaction between laser radiation and graphite surface, intensive surface destruction and process extinction after the end of laser impact. Characterizations of ablation plume such as angle of distribution, particles velocity and ablation plume delay relatively to laser beam impaction moment were carried out with high temporal resolution.

References
STRUCTURE AND ULTRAFAST DYNAMICS OF LASER-GENERATED DISORDERED STATES OF MATERIALS

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Time-resolved diffuse X-ray scattering with 50 fs, 9.5 keV X-ray pulses from the Linear Coherent Light Source was used to study the structural dynamics in materials undergoing melting and ablation after fs laser excitation.

1. Introduction

Irradiation of solid materials with intense fs laser pulses can induce phase transitions on very short time scales, and often along non-equilibrium pathways. The advent of ultrafast diffraction techniques has made it possible to directly follow the associated structural changes with spatial and temporal atomic scale resolution. This contribution will report about experiments carried out at the Linear Coherent Light Source (LCLS) where we applied time-resolved diffuse X-ray scattering to study the structural response of materials undergoing melting and ablation after strong fs excitation.

2. Time-resolved diffuse X-ray scattering at the LCLS

Thin films (25 - 100 nm thickness) of solid materials deposited onto free standing Si3N4-membranes, have been irradiated by 50 fs, 800 nm optical laser pulses at fluences sufficient to melt and ablate the material. Subsequently the scattering of a time-delayed 50 fs, 9.5 keV X-ray pulse from the LCLS has been observed in normal-incidence transmission geometry. The time-resolved measurements covered a large range of scattering angles corresponding to a momentum transfer $q = 4\pi/\lambda \sin(\theta/2)$ from 0.04 Å⁻¹ < q < 5 Å⁻¹. The scattering data provide, therefore, information about the transient structural changes of the irradiated material on different length scales. Laser-induced melting as well as the structural dynamics after disordering has been investigated for different classes of materials (metal: Au, semimetal: Bi, semiconductor: Ge) over a wide time- and fluence-range and will be presented.

3. Results

3.1 Laser-induced melting

As a first example we discuss the melting dynamics in laser-excited Bi. Fig. 2a (left) shows in a false color representation the transient diffraction pattern I(q) as a function of delay time of a 25 nm Bi-film undergoing melting after excitation at a fluence of 25 mJ/cm² (note the logarithmic time-axis and the zero delay offset by 0.7 ps).

![Fig. 2: Left: False-color representation of the transient diffraction pattern I(q,Δt) of laser-excited Bi; Right: Line-outs in the vicinity of liquid structure factor peak around 2.1 Å⁻¹ for selected delay times.](image)

At these high fluences well above the melting threshold the material melts non-thermally within a few hundred fs as indicated by the rapid decay of the two diffraction peaks of the solid phase at 3.3 Å⁻¹ and 4.6 Å⁻¹. On the same time-scale a broad diffraction feature appears at 2.1 Å⁻¹, indicative of the formation of the disordered liquid state. Moreover, as can be clearly seen in Fig. 1b (right), the position as well as the shape of the liquid structure factor peak changes with time. While Ge shows a similar fast non-thermal melting transition, Au melts only thermally on ps time-scales. Both, Ge and Au exhibit similar to Bi pronounced structural dynamics in the liquid phase.
3.2 Femtosecond laser-ablation

Laser ablation describes the permanent removal of macroscopic amounts of material from a laser-irradiated surface. For ablation induced by ultrashort laser pulses it is believed that subsequent to the initial fast heating and disordering rapid adiabatic expansion can push the material into meta-stable or even unstable regions of the state diagram leading to its disintegration and transition into a volatile state. However, the underlying processes are still not well understood and different ablation mechanisms like spallation, phase explosion and fragmentation have been invoked (i.e. [1-5]).

We used time-resolved X-ray scattering at small scattering angles (0.04 Å⁻¹ < q < 0.6 Å⁻¹) to follow the formation of nm length scale inhomogeneities expected to occur during the ablation process. In agreement with these expectations and with our earlier experiments performed with much lower X-ray flux at the SPPS [6] we observe a strong transient small-angle scattering signal. Fig. 2 shows an example data obtained on a 100 nm thick, laser-excited Au-film (Left side: Fluence-dependencies for different delay times; Right: Time-dependencies for two different fluences).

![Graph showing X-ray scattering data](image)

Fig. 2: X-ray scattering at small angles (0.04 Å⁻¹ < q < 0.6 Å⁻¹) of a 100 nm thick laser-excited Au-film. Left: Scattering signal as a function of fluence for time delays of 100 ps (red) and 500 ps (blue). Right: Normalized scattering signal as a function of delay time for laser fluences of 0.75 J/cm² (red) and 2 J/cm² (blue).

The data presented in Fig. 2 exhibit two remarkable features: (1) The scattering signal at small scattering angles is only observed for fluences above a threshold value of $F_{th} = 0.5 \text{ J/cm}^2$. This fluence coincides exactly with the ablation threshold (i.e. threshold for crater formation) as determined by a post-mortem analysis of the final structural modifications of the irradiated film. (2) The scattering signal is delayed with respect to the excitation and occurs after melting of the material. Moreover, the delay depends on excitation fluence, as evidenced by the time-dependent data presented in the right graph. For 2 J/cm² (well above threshold) the scattering signal can be observed only for delay times larger than 100 ps. For 0.75 J/cm² (close to threshold) it sets in much earlier (∼20 ps). In line with this we find that for early delay times ($\Delta t = 100$ ps) the small angle scattering is only observed for fluences in a limited range above threshold, while for later delays ($\Delta t = 500$ ps) it increases continuously with fluence. Similar results (i.e. threshold behavior, delayed onset) have been obtained on thin Bi-films.

These observations give clear evidence that ablation is responsible for the appearance of the small angle scattering signal. However, the pronounced differences for low and high fluences indicate different ablation mechanisms in the different fluence regimes. Results of recent molecular dynamics simulations [3-5] suggest that close to the threshold the rapid adiabatic expansion puts the material under strong tensile stresses (negative pressure). When the tensile strength is exceeded the material simply tears apart. Therefore, ablation can be described as a spallation process and is of mechanical nature.

Within this picture a very simple prediction can be made for the case of a homogeneously heated film (as in our experiment): Spallation will start when the two rarefaction waves propagating from the film boundaries into the film meet in its center, that is $t_{\text{spall}} = d/2c_S$ (d: film thickness, $c_S$: sound velocity). Using the known film thickness $d = 100$ nm and the published value of the sound velocity of liquid Au $c_S = 2.567$ km/s [7] we calculate $t_{\text{spall}} = 19.5$ ps, exactly what we measure in the experiment for the onset of the small angle scattering in the fluence regime close to the threshold.

For higher fluences the simulations predict that expansion occurs at positive pressure and ablation by explosive boiling/phase explosion or fragmentation [3,4]. However, to our knowledge none of the simulations has made a direct comparison of the time-scale for the onset of ablation in the different fluence regimes or predicted such a difference as we see it in our measurements.

References

FLICKER-NOISE SPECTROSCOPY ANALYSIS OF MAGNETOENCEPHALOGRAM SIGNALS IN DIAGNOSIS AND TREATMENT OF PHOTOSENSITIVE EPILEPSY

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Our study demonstrates the potential of flicker-noise spectroscopy (FNS) analysis of neuromagnetic brain responses (magnetoencephalogram, MEG) in possible diagnosis of and estimating the effectiveness of treatment of photosensitive epilepsy. A two-parameter FNS cross-correlation function is applied to show that the breakdown of frequency-phase synchronization in the MEG signals of the patient can be attributed to two distinct mechanisms: high-frequency resonances (50-100 Hz) at specific brain areas and changes in high-frequency stochastic components for other brain areas. Our analysis also reveals a certain disruption of regular behavior and occurrence of asymmetry in three-dimensional plots of the cross-correlation function for some healthy controls, suggesting that these individuals may be susceptible to photosensitive epilepsy.

Frequency and phase synchronization, manifestation of specific correlations between characteristic frequencies and phases of the excitations in different regions of the brain (specific neural ensembles), and synchronization of the excitation amplitudes are the necessary conditions for the brain to function as an integral system [1, 2]. A normally functioning brain responds to external actions on the human organism by establishing some optimal level of such correlations. A significant deviation from this optimal level, such as an anomalously high level of synchronization or lack of synchronization, may be considered as an indicator of a pathology in brain activity.

We suggest that the following two-point cross-correlation function, introduced within the framework of flicker-noise spectroscopy (FNS) [3, 4], is an effective tool for analyzing the correlations between signals $V_i(t)$ and $V_j(t)$ simultaneously measured at points $i$ and $j$ of the scalp, for example, electroencephalograms (EEG) or magnetoencephalograms (MEG):

$$q_{ij}(\tau, \theta) = \left\langle \frac{V_i(t) - V_i(t + \tau)}{\Phi^{(2)}(\tau)} \left[ V_j(t + \theta) - V_j(t + \theta + \tau) \right] \right\rangle_{\tau \rightarrow |\tau|},$$

where $T$ is the averaging interval, $\tau$ is the “lag time” (we assume $\tau \geq 0$); $\theta$ is the “time shift” parameter. The cross-correlation expression $q_{ij}(\tau, \theta)$ is a function of temporal parameters $\tau$ and $\theta$, which can be represented as a three-dimensional plot. Of most interest for the analysis are the intervals of $\tau$ and $\theta$ where the cross-correlation function $q_{ij}(\tau, \theta)$ approaches positive unity (maximum level of positive correlations) or negative unity (maximum level of negative correlations). The value of $\theta$ corresponding to maximum values of cross-correlation $q_{ij}(\tau, \theta)$ characterizes the cause-and-effect relation (“flow direction”) between signals $V_i(t)$ and $V_j(t)$. When $\theta > 0$, the flow moves from point $i$ to point $j$, when $\theta < 0$, from $j$ to $i$. When the distance between points $i$ and $j$ is fixed, the value of $\theta$ can be used to estimate the rate of information transfer between these two points.

Our previous studies show that the analysis of cross-correlations by Eq. (1) for sets of MEG/EEG signals can identify and quantify the effects of frequency-phase synchronization in the brain, which may be essential for the diagnosis of psychiatric disorders (schizophrenia) as well as some neurological and neurodegenerative diseases [5-7]. For instance, the FNS cross-correlation function was used for the analysis of the MEG signals recorded as the neuromagnetic response from a group of healthy human participants ($N=9$) and a patient (a 12-year girl) with photosensitive epilepsy (PSE) while they were viewing equiluminant flickering stimuli of different color combinations (RB – red-blue and RG – red-green) [6, 7]. Photosensitive epilepsy is the occurrence of high neural activity in the form of epileptic spikes in response to triggering visual stimuli, particularly flickering light, which is accompanied with various clinical and paraclinical manifestations. The interest to such analysis was initiated, in particular, by the perceived potential danger of modern cartoons to provoke PSE in children and adults. The experimental data were generated by 61 SQUID (superconducting quantum interference device) sensors attached to different points around the head, which can record weak magnetic induction gradients of about $10^{-11} - 10^{-10}$ T/cm [2, 8, 9]. The sampling frequency $f_s$ of MEG signals was 500 Hz. It was found that the power spectrum of the signals in the patient contains
a significant high-frequency component at approximately 50 Hz, and for sensors 10 (frontal lobe), 59 (central zone), and 46, 51, 53 (forehead) an additional frequency component at approximately 100 Hz, both of which are not seen in the data for healthy subjects. The cross-correlation function (1) demonstrated a breakdown of frequency-phase synchronization for some cortex areas in the patient, which was not seen in the control subjects. The highest level of the breakdown was reached at the cortex areas in the proximity of the abovementioned “anomalous” sensors, which implies that the pathological mechanisms of PSE may be localized there. It was concluded that the disruption of cross-correlations in these cortical regions, which is associated with the suppression of cortical regulatory functions (frequency and phase synchronization) when external actions exceeding a certain “dangerous” threshold are applied, is the main indicator of the pathological changes taking place in the PSE patient. This implies that the cross-correlation analysis by formula (1) may be used not only for identifying the pathological changes but also for developing therapeutic methods and estimating the efficiency of the medical treatment of PSE.

The current study demonstrates that the analysis of neuromagnetic responses from the cortical regions in the proximity of “anomalous” sensors, though sufficient for diagnosing PSE, cannot be used by itself to control the efficiency of medical treatment. This is due to the fact that the breakdown of frequency-phase synchronization is not always associated with the onset and amplification of high-frequency (50÷100 Hz) neuromagnetic responses. For example, sensors 37, 25 (left temple area) and 30 (left parietal area) show a disruption in natural cortical rhythms not because of high-frequency resonances (50÷100 Hz) but due to a higher intensity of high-frequency stochastic components, which is agreement with study [1]. To characterize the intensity of stochastic components, we use the “spikiness” parameter $S_{T_0}$, which is defined in FNS as the power spectrum value at the frequency corresponding to the characteristic time $T_0$ of loss of correlations in the series of high-frequency irregularities. We report that for the patient the values of spikiness factor at sensors 25, 30, 37 and the anomalous sensors are 3 or more (up to 10) times higher than the maximum values of $\sim 150 \, fT^2/fd^2/cm^2$ for control subjects.

It should be noted that our analysis also uncovered a certain disruption of regular behavior and occurrence of asymmetry in the 3D dependences of cross-correlation function $q_{ij}(\tau, \theta_{ij})$ for some healthy subjects, which suggests that those individuals are susceptible to PSE. At the same time, we found that certain cortical areas in the patient (for example, at sensors 21 and 54) are not involved in the high neural activity under the action of flickering-color stimuli.

This study shows that the identification of the level of breakdown in frequency-phase synchronization of MEG and EEG signals in different cortex areas using FNS cross-correlation function (1) may be used not only as a diagnostic sign of neurodegenerative diseases and psychiatric disorders but also to assess the effectiveness of therapeutic actions, which is in agreement with our previous studies [5-7]. The tendency of the organism to restore the synchronization to its normal levels is considered as the cornerstone of the analysis. We believe that a similar cross-correlation analysis based on appropriate biomedical signals may be used to assess the effectiveness of medical treatment for other diseases and conditions.

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**References**

Along with high longitudinal resolution of optical coherence tomography, confocal optical coherence microscopy (OCM) provides high transversal resolution due to relatively high numerical apertures. However, the presence of relatively high numerical apertures leads to limited depth of field, which reduces the speed of OCM and decreases the advantage of Fourier domain detection. In this paper we propose a numerical processing technique for three-dimensional image reconstruction in Fourier domain OCM. It takes into account not only the defocus of different parts of imaged volumetric sample, but also the effects of upper layers’ refractive index on imaging the sample inner structure. Besides providing sharp coherence gated imaging, this technique also allows for determining both the geometrical thickness and refractive index of the sample layers.

1. Temporal and angular spectrum gating in low-coherence interferometry

Low-coherence interferometry techniques allow three-dimensional imaging of semitransparent samples, based on longitudinal coherence gating, and are widely used in biomedicine. In low-coherence interferometry the longitudinal coherence gating effect is caused by two factors: temporal and angular spectrum gates. Conventional optical coherence tomography (OCT) utilizes wide temporal spectrum and narrow angular spectrum of the optical field. Wide temporal spectrum leads to high longitudinal resolution, while narrow angular spectrum provides large depth of field. However, this narrow angular spectrum (due to low numerical apertures (NA)) leads also to low transversal resolution. To obtain high transversal resolution, higher numerical apertures are used, which provide wider angular spectrum of the optical field. However, wide angular spectrum results in small depth of field, which is in fact narrow longitudinal angular spectrum gate. This is the case of confocal optical coherence microscopy (OCM). So, one has to choose between imaging with either large depth of field and low transversal resolution or small depth of field and high transversal resolution.

To overcome this limitation in OCT, in Ref. [4] a numerical processing technique was proposed, based on synthetic aperture approach and inverse scattering analysis. It was shown to allow sharp sample imaging not only within the original depth of field, but also in defocused regions. However, in Ref. [4] the effects of refractive indices of upper sample layers on imaging its inner structure were not taken into account. Meanwhile, in a number of works it has been shown, that refractive index of the sample layers affect differently the location of temporal and angular spectrum gates. Mutual shift of these gates due to the mismatch of refractive index in sample and reference arms of an interferometer, leads to fading of the coherence signal. This effect limits applicability of the technique, described in Ref. [4], to imaging samples with uniform refractive index, equal to that of the immersion.

In Ref. [5,8] it has been shown, that this effect of coherence signal fading due to refractive index mismatch can be overcome in confocal and full-field arrangements by mechanical shifting of the temporal and angular spectrum gates. Along with sharp coherence gated imaging, it was shown to allow determination of both geometrical thickness and refractive index of the sample layers. However, the need for mechanical scanning makes these techniques time consuming and limit their applicability to in vivo imaging.

Recently, we developed a theoretical model of interference microscopy imaging to provide analysis of the imaging process of different types of samples in different types of interference microscopes. Basing on this theory, we propose in the current paper a numerical processing technique, which is intended to overcome the problems of coherence gate fading in confocal OCM imaging and allow fast three-dimensional imaging of samples, which may consist of layers with different refractive indices.

2. Description of the numerical processing technique

Let us consider a Fourier domain OCT/OCM system, which performs imaging a layered sample with layers widths $\Delta z_j$ and refractive indices $n_j$ at a number of temporal frequencies $\omega_i$, and scans the sample transversal position by displacement $(x_d, y_d)$ (realized via displacement of the sample itself or by transversal scanning the light beam). To obtain sharp coherence gated images of the sample interface, located under $N$ sample layers, we should calculate the
spatial spectrum $\hat{F}(w_0,k_y,k_y)$ of the coherence signal $\Gamma(w;x,y)$ and divide it by certain correction function $\Xi(w_0,k_y,k_y)$. Fourier transformation of the resultant function $\hat{F}(w_0,k_y,k_y)/\Xi(w_0,k_y,k_y)$ and integration over the temporal spectrum yields sharp coherence gated image of the interface of interest. Results of numerical simulation, illustrating this numerical correction procedure, are presented in Fig. 1.

Fig. 1. Numerical simulation of imaging a layered sample in confocal OCM. The sample surface is in focus; the interface of interest is located under two layers with widths 20µ and 15µ and refractive indices 1.33 and 1.1 respectively; $n_d=1$, NA=0.3, illumination field fills the whole objective aperture, central frequency of illumination field $w_0=2.36 \times 10^{15}$ Hz (corresponds to $\lambda_0=800$ nm), spectrum width $\Delta w=3.53 \times 10^{14}$ Hz. a) actual distribution of the reflection coefficient on the interface; b) image of the interface, reconstructed with only temporal spectrum gate shifting according to conventional OCT/OCM principle; c) image of the interface, reconstructed according to the proposed technique. The field size for all images is 154×154 µm.

When only the temporal spectrum gate is shifted to the interface position, the resultant image is sufficiently blurred (Fig. 1b). However, when numerical processing based on the proposed technique is applied, the reconstructed image of the interface of interest appears sharp, though no mechanical refocusing was done (Fig. 1c). Little blurring in Fig. 1c compared to Fig. 1a is due to the intrinsic diffraction limitation caused by finite size of the imaging aperture.

It can be shown that geometrical thickness and refractive index of the sample layers affect differently the correction function $\Xi(w_0,k_y,k_y)$. Thence applying appropriate processing, we can determine separately the geometrical thickness and refractive index of the sample layers similarly to Ref. [5], but without the need for mechanical scanning of the focus position and optical delay of the interferometer.

References
This paper presents a nanoparticle-free approach to manufacture a phantom with optical properties close to those of biotissues. Good reproducibility and optical homogeneity together with the convenient, easy-to-implement manufacturing procedure make this approach a potential candidate to become a biotissue phantom standard in the field of biophotonics.

1. Introduction

Increasing interest in optical techniques for noninvasive biomedical diagnostics and therapy leads to development of new methods and devices. An important phase of such development is validation of created systems, proposed methods and theoretical predictions. For verification of newly developed tools, a special kind of samples with well-controlled optical properties that closely match those of biotissues is required. Numerous phantoms were proposed preliminary [1], but none of them has become a standard yet.

In this work, we present a novel nanoparticle-free biotissue phantom made on the basis of silicone elastomer. Convenient manufacturing procedure, stable and uniform optical properties close to the optical properties of biotissues in the near infrared spectral range (e.g. human or porcine dermis [2]) are the main advantages of the considered phantom.

2. Materials and methods

Two-component Sylgard® 184 silicone elastomer (Dow Corning corp.) was chosen as a main material for the phantom preparation. This substance was previously used for the phantom manufacturing using the traditional nanoparticle-based approach [3]. Both of the components (the base and the curing agent) are transparent viscous liquids. The mixture of the base and the curing agent at the ratio of 10:1 respectively is capable of curing at room temperature. Typically, 24 h is needed for complete solidification under such conditions. Faster curing at higher temperatures is also possible. As a result, we have elastic and highly transparent material which is frequently used in the field of electronics as a dielectric.

In our study, the base and the curing agent were mixed with glycerol (Sigma-Aldrich corp.) at the ratio of 10:1:10, respectively. Due to the chemical reaction this mixture became opaque. After the careful stirring, the mixture was poured into the metal cuvette to form a slab of certain thickness. By the combination of such blocks with the modified optical properties (e.g. by adding absorber) the formation of the multilayer phantom is also possible.

3. Results

Preliminary characterization of the phantom was performed by the scanning electron microscopy (SEM), see Fig. 1. In this picture, a spongy structure of the manufactured phantom is clearly seen. Obviously, the cavities of this structure serve as scatterers for light. The size distribution of the phantom cavities is also shown in Fig.1. The averaged cavity diameter in this case is ~4 µm.

Further, thin slices (100 and 300 µm) of this material were tested with the optical coherence tomography (OCT) technique (results are not shown). For this purpose, a spectral-domain, SLD-based OCT setup (Thorlabs, USA) providing the axial resolution of ~6 µm at the central wavelength of 930 nm was used. Good uniform volume distribution of the optical properties was confirmed. Additionally, the refractive index of the phantom was calculated as...
a ratio between its optical and physical thicknesses. For the tested sample, the refractive index was 1.44 that is closely matching the refractive index of the human or porcine skin. The attenuation coefficient of the phantom was preliminary estimated from the slope of the OCT signal using the single scattering approximation [4] which is valid for thin layers. In our case, the attenuation coefficient was of 10.1 mm⁻¹. Full-scale study of the optical properties of the manufactured phantoms was performed using the spectrophotometer with the integrating spheres (Optronic Laboratories, USA). Diffuse reflectance, diffuse transmittance and collimated transmittance were measured for the spectral range of 350-1100 nm. Optical properties were retrieved by using the inverse adding-doubling method developed by S.A. Prahl [5]. The results of the calculations are shown in Fig. 2.

![Graph showing optical properties](image)

**Figure 2:** Optical properties of the manufactured phantom retrieved by the inverse adding-doubling method from spectrophotometer measurements.

From this figure, we can see that the estimated scattering coefficient of the manufactured phantom is of ~10 mm⁻¹ and stays quite constant over the whole considered spectral range. Thus, we can see that the spectrophotometer measurements confirmed the estimation of the attenuation coefficient from the slope of the OCT signal that ensures mutual reliability of our measurements. Some uncertainty is possible in the UV and visible range due to the difference in the reflective index. The refractive index estimated for the near infrared range is used in the calculations for the other ranges because no other data are available. Beneficial is a relatively high anisotropy factor since most of biotissues have it in the range 0.7-0.9. To further characterize the phantom, we have measured the speed of sound by the pulse-echo method. The measured value is of 1.25 mm/μs which is a bit lower than the speed of sound in biotissue (~1.4 mm/μs) [6].

Thereby, we have demonstrated easy-to-use, nanoparticle-free method to fabricate a biotissue phantom with the optical properties close to the optical properties of biotissues in the near infrared spectral range (e.g. human or porcine dermis [2]). Since no nanoparticles are used, no problems occur following their uncontrollable aggregation, sedimentation and nonuniform distribution over the volume of the phantom. No skin effect (reduced scatterers concentration in the subsurface region) was also observed. Thus, we believe that this approach could become a standard for the tissue (first of all skin) mimicking phantoms in the field of biophotonics.

**References**

EFFECT OF CARBON NANOPARTICLES ON MICRORHEOLOGICAL PROPERTIES OF HUMAN AND RAT BLOOD BY MEANS OF LASER EKTACYTOMETRY AND AGGREGOMETRY

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The aim of this work is the investigation of the effect of nanodiamonds and fullerenes on the microrheology of the human and rat blood after incubation of the blood samples with nanoparticles. In vitro measurements were carried out by means of laser ektacytometry and aggregometry techniques. Decrease in deformability and alteration of aggregation parameters of red blood cells starting with certain critical concentrations of nanoparticles is demonstrated.

1. Introduction

Biocompatible carbon nanoparticles (nanodiamonds (ND) and fullerenes) can potentially be used for various biological and bio-medical applications because they are not toxic and do not destroy vitally important organs, tissues and cells. It is presumed that in order to reach the target these particles would be administered into blood. However, so far there is little information on the interaction of ND and fullerenes with major blood components: cells and plasma proteins. It can be assumed that interaction with nanoparticles can affect the red blood cells (RBCs) properties such as their ability to change their shape under shear stress when propagating along blood vessels and capillaries. The aim of this work was to study the in vitro effect of fullerenes and ND on blood microrheology properties, in particular, on the ability of RBC to deform in shear flow characterized by shear stress dependence of the deformability index and on their ability to spontaneously aggregate in whole blood characterized by the time of linear and three-dimension aggregates formation.

2. Materials and methods

In this work, we conducted measurements with Laser Aggregometer – Deformometer of Erythrocytes – LADE-6 (RheoMedLab, Russia). Operation of this device is based on laser aggregometry and diffractometry techniques [1, 2]. Its schematic layout is shown on Fig. 1.

Figure 1: Schematic layout of experimental setup: 1,9 - diode lasers, 2 – Couette chamber, 3 - mirror, 4 - motor, 5 - CCD, camera, 6 - PC, 7 - lens, 8 – photodetector.
2.1. Laser aggregometry technique
The essence of laser aggregometry is in measuring the kinetics of the intensity of light backscattered from a sample of whole blood placed into the Couette chamber during spontaneous aggregation of RBCs related to the aggregation kinetics [2]. The obtained kinetics curves are approximated by a sum of two exponential functions where the exponential coefficients are related to the characteristic times of linear ($T_1$) and three-dimensional ($T_2$) aggregates formation.

2.2. Laser ektacytometry (dиффрактометрия) technique
The essence of laser diffractometry is in obtaining and subsequent analysis of the obtained diffraction pattern from a highly diluted suspension of RBCs at rest and shear flow [1, 3 and 4]. Suspension of RBCs is placed into the gap between two coaxial cylindrical thin-walled cups made of optical plexiglass (Couette chamber). The outer cup can be rotated relative to the inner one at stepwisely changed speed. The deformation of RBCs under shear stress results in stretching of the diffraction pattern in the direction perpendicular to the flow velocity vector. The shape of the diffraction pattern becomes elliptical. Deformability index (DI), defined as ratio of the difference between major and minor axes of the ellipse that approximates the line of equal intensity of the diffraction pattern to their sum, is measured for a number of stepwisely changed shear stresses. Dependence of the DI on shear stress characterizes the ability of red blood cells to deform passing through the thin blood vessels and capillaries.

2.3 Sample preparation
In our experiments, we incubated the samples of freshly drawn blood with suspensions of ND with sizes from 5 to 500 nm in bi-distilled water in concentrations 33 and 100 µg/ml or with aqueous solutions of water soluble Fullerene in concentrations from 1.0 to 5000 µg/ml. Each sample of whole blood was incubated with nanoparticles during 1 hour. We also tested the nanodiamonds with carboxylated surfaces (cND) and compared their effect to that of ND.

We performed several series of in vitro measurements of the DI and parameters of aggregation kinetics with human and rat blood samples with different types of particles, sizes and different concentrations mentioned above. In the experiments with human RBCs we investigated blood samples from 7 volunteers for each type and concentration of particles. In the experiments with rat RBCs we investigated blood samples from 7 rats for each type and concentration of nanoparticles. All blood samples were stabilized with EDTA to prevent blood clotting. All measurements were performed within two hours after blood drawing.

3. Results and conclusions
We found that 1 hour-long incubation of RBC with both nanodiamonds and fullerenes results in the alteration of both deformability index and aggregation kinetics of RBC. The effect is concentration dependent. For example, smaller NDs and cNDs (around 5 nm average size) in smaller concentrations decrease the time of formation of both linear and 3D RBC aggregates. Larger NDs and cNDs (around 500 nm characteristic size) as well as smaller ones in higher concentrations lead to less pronounced negative effects which can be speculated as a result of small nanoparticles aggregation in concentrated suspensions and inability of relatively large nanoparticles and their aggregates to penetrate into the RBC through their membranes. Carboxylation of ND particle surface makes the negative effect of smaller cNDs less pronounced but does not totally eliminate it.

The effect of nanodiamonds and fullerenes in high concentrations (higher than 2 mg/ml for fullerenes and 30 µg/ml for ND) on the deformability of RBC in shear flow is negative as well: the cell deformability index is reduced all through the range of tested shear stresses (from 3 to 60 Pa). The reduction of the deformability index is more pronounced at higher concentrations of the nanoparticles (around 100 µg/ml for nanodiamonds and 5-25 mg/ml for fullerenes).

Basing on these results one can conclude that the nanodiamonds and fullerenes can be used as an effective bio-labeling tool in ambient conditions at low concentrations, without complicating the blood’s physiological conditions. However, controlling the deformability properties of RBCs and rheological properties of blood is necessary during treatment.

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References
The toxic effect of heavy metals over the living organisms is known to arise from the alternation of the course for biological reactions in cells. One of such violations appears to be the process of supra-molecular structures formation, for example, the dipole protein nano-clusters in blood. This phenomenon can be well studied in the biological solutions, such as blood serum, or a widely adopted normal saline solution of enzymes.

Thus the important role in categorize heavy metals is played by following conditions: their high toxicity for live organisms in rather low concentration, and also ability to bioaccumulation. Almost all heavy metals (except for lead, mercury, cadmium and the bismuth which biological role currently is not clear), actively participate in biological processes, are a part some many enzymes.

In this work was studied the effect of ions some metals (K⁺, Na⁺, Pb²⁺, Fe³⁺, Eu³⁺) on enzymes (pepsin, collagenase, lysozyme, creatine kinase) in water solutions.

The results of our experiments has shown that charged macromolecules dynamic properties and radii of formed scattering particles in solutions essentially depend on net charge condition of enzymes and can be used for diagnostics and control.

For macromolecules solutions it is possible to connect a normalized autocorrelation function of light scattering intensity with a translation diffusion coefficient:

\[ g^{(1)}(\tau) = \exp(-D_t q^2 \tau) \]  

(1)

In our study, scattering properties of water enzyme solutions were investigated by the automatical set-up element and a scattered radiation photoelectron detector.

It was found that cluster formation depends on metal ion radius

The nature of interaction enzyme macromolecules in case when the solution contains metal ions with a large ionic radius depends largely on dipole-dipole forces. Enzyme molecules may come extremely closely to one another to form a macromolecular complex-a dipole cluster

The mass and radius of enzyme clusters forming in the solution increases by more than one order of magnitude as compared to the mass of a macromolecule and reaches its maximum near the isoelectric point of enzyme.

The appearance of cluster cans disturbance metabolic processes in the cells, membranes, tissue.

Cluster formation process can explain toxic influence of heavy metal ions at the very small concentration on the living organisms

Especially influence on some protein like albumins, globulins, collagen, lysozyme and so on has the potassium. K⁺ ions presence in the protein solutions also induced appearance of dipole protein nano-clusters.

References

INVESTIGATION OF PROTEINS AGGREGATION
IN WATER SOLUTIONS CONTAINING HEAVY METAL IONS
WITH LASER FLUORESCENCE METHODS

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In the solutions of bovine serum albumin, collagen and γ-globulin the translation and rotary diffusion coefficients dependences from pH and concentration of Pb2+, Cs+, Rb+ and K+ ions have been received by methods of Fotonno-correlation spectroscopy and Polarized Fluorescence. It is revealed that the size of ionic radius of metal influences on intermolecular interactions and mobility of protein molecules in solutions. Potassium ions have the big ionic radius and behave similarly heavy metals. They could lead to aggregation of protein molecules near isoelectric point.

A method used in this work bases on polarization of fluorescence upon the laser excitation in the ultraviolet (UV) wavelength range. This method was exploited to study toxic effects of lead, potassium, rubidium and cesium ions over water solutions of bovine serum albumin (BSA), γ-globulin and collagen. All studies were performed at the isoelectric points of serum albumin (pH 4.9), γ-globulin and collagen (pH 6.0).

Preliminary, there were obtained fluorescence spectra of the tryptophan amino acid water solutions in the presence of the Pb2+ ions. It should be noted, that fluorescence intensity of tryptophan is not effected by the concentration of the lead salt, even when there is a tenfold exceed of it over the concentration of amino acid.

In our earlier works [1,2] fluorescence spectra of BSA were studied in water solutions containing NaCl and KCl salts. It was found that Na+ ions do not alternate intensity of albumin fluorescence spectrum, whereas K+ ions cause decrease in fluorescence intensity.

In BSA, γ-globulin and collagen water solutions the presence of Na+ ions (with concentration ca. the physiological value) does not effect polarization degree of fluorescence, but the degree increases when adding Pb2+, Cs+, Rb+ or K+ ions (with concentrations ca. MPC). This phenomenon indicates the changes in dynamic properties of proteins macromolecules such as the correlation time of rotational mobility and, consequently, the mass of the particles.

These results draw to a conclusion that fluorescence quenching occurs only in case when amino acid is a part of protein compound. This effect is due to the facts that lead, potassium, rubidium and cesium ions are strongly associated with negative groups on protein surface, and that the nature of macromolecules interaction changes resulting in protein clusters formation.

References:
Gadoteric acid and gadodiamide molecules have gadolinium-containing chelate structures that are used in magnetic resonance tomography. [1]. Over the past two decades, they were considered safe and effective for medical imaging. However, recent results indicate the presence of gadolinium in the skin and soft tissues in patients with renal insufficiency, even with the current hemodialysis [2]. Nephrogenic systemic fibrosis (NSF), which was described in 1997, is a recently discovered rare disease of unknown etiology that affects patients with renal insufficiency. The development of NSF was directly linked to the influence of gadolinium-containing magnetic resonance contrast agents in 2006 [3].

This work is devoted to the study of main blood protein - albumin interaction with gadolinium-containing chelates. In this regard, it became interesting to study the nature of molecular motion and intermolecular interactions in water solutions of biological macromolecules (albumin) under the influence of various external factors (pH, concentration of macromolecules, temperature, metal ions, gadolinium-containing chelate complexes). As a result of this work were studied changes of serum albumin dynamic parameters under the influence of gadolinium-containing chelates (gadoteric acid and gadodiamide). First identified the physical mechanism of toxicity of gadolinium ions belonging to the chelated structure of gadoteric acid on serum albumin.

The method of photon correlation spectroscopy was used and the following experimental results were obtained:

1) The dependence of translational diffusion coefficient $D_t$ (pH) for the pure water solution of albumin (Fig. 1, curve 1), for albumin water solutions with addition of gadoteric acid (Fig. 1, curve 2) and for albumin water solutions with addition of ferric chloride (Fig. 1, curve 3). Depending on the data $D_t$ (pH) are similar in character and values, and also have a form close to parabolic.

2) When adding two impurity substances in albumin water solutions (gadoteric acid and ferric chloride) $D_t$ decreases. With increasing ionic strength of ferric chloride at a fixed concentration of gadoteric acid in albumin solution translation diffusion coefficient decreases (Fig. 2).

![Figure 1: Dependence of the translational diffusion coefficient of the pH in water solution of pure albumin (curve 1), with the addition of gadoteric acid (I = 0.05 mg / ml) (curve 2), with the addition of salts of ferric chloride FeCl$_3$ (I = 0.004 mol / L) (curve 3).](image-url)
Figure 2: Dependence of the translational diffusion coefficient of the pH in water solution of pure albumin (curve 1) and water solutions of albumin with the addition of two impurity substances - gadoteric acid (I = 0.05 mg / ml) (curve 2, 3, 4) and salts of ferric chloride FeCl$_3$, I = 0.001 mol / L (curve 2), I = 0.002 mol / L (curve 3), I = 0.004 mol / L (curve 4).

References
MICROSURGERY OF CELL MEMBRANE WITH FEMTOSECOND LASER PULSES FOR CELL FUSION AND OPTICAL INJECTION

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We report on results of using femtosecond laser scalpel for microsurgery of plasma membrane of living cells. Femtosecond laser pulses were used to initiate cell fusion as well as to perform reversible permeabilization of cell membrane required for efficient injection of extrinsic substances into single living cells. Laser-based cell fusion of mammalian embryo blastomeres as well as fusion of cell bodies of neurons of mollusc Limnaea stagnalis were successfully carried out by applying single femtosecond laser pulses (Cr:Forsterite seed oscillator and regenerative amplifier (Avesta Ltd.), 1240 nm, 100 fs, 10 Hz) with energies of 30-35 nJ per pulse. It was shown that the fusion of cells was completed within 5-60 minutes depending on the cell type. Ultrashort Ti:sapphire laser pulses (MIRA-Seed (Coherent), 800 nm, 60 fs, 80 MHz, 2-4 nJ per pulse) were also applied to perforate the plasma membrane of living cells and inject various fluorophores as well as nucleic acids. In both cases the energy of laser pulses was thoroughly optimized to obtain high viability of treated cells and high efficiency of the procedures of cell fusion and optical injection.

1. Introduction

Cell microsurgery with ultrashort laser pulses has become an important tool in various biological studies and medicine. Femtosecond (fs) lasers are widely used for high resolution imaging of cells and tissues, for corneal surgery in ophthalmology, for efficient caries removal in dentistry. One of the most promising applications of femtosecond lasers is dissection of cellular organelles and selective permeabilization of cell membrane, so-called optical perforation (optoinjection, optoporation), enabling introduction of foreign reagents and compounds into cells. In this paper we demonstrate the possibilities of reversible and irreversible cell membrane perforation with femtosecond laser pulses that can be effectively used for cell fusion and optoinjection of different extrinsic substances into living cells.

2. Femtosecond laser-based cell fusion

Using of laser enables performing cell fusion with high selectivity if compared to standard fusion techniques that utilise chemical reagents or electric fields to initiate cell fusion. Laser-based cell fusion requires optimization of various parameters, such as laser pulse energy, exposure time or focus adjustment. To simplify the optimization and adjustment of the parameters we used 2-cell mouse embryos for cell fusion according to the fact that there was a well-defined interface between two blastomeres at that developmental stage of the preimplantation embryo. It can be easily visualized, exposed to laser radiation and controlled during the fusion process. Central region of plasma membrane in the interface was exposed to femtosecond laser pulses at a wavelength of 620 nm (second harmonic generation, Cr:Forsterite seed oscillator and regenerative amplifier (Avesta Ltd.), 1240 nm, 100 fs, 10 Hz). Application of a single femtosecond laser pulse gently ruptured membrane and initiated the merging of the two blastomeres into one (Fig.1). Cell fusion process was usually completed within 30-60 minutes. Fused blastomeres were placed in an incubator and cultured until the blastocyst stage. Finally, the hybrid embryos were stained with Hoechst 33258 and Propidium Iodide and viewed under fluorescent microscope to estimate the survival rates of treated embryos. It was determined that cell fusion occurred when energy of laser pulses was in the range of 30-50nJ. Peak intensity in these cases was close to 10¹³W/cm². Laser-induced optical breakdown is supposed to be the main mechanism for the membrane perforation. Instead of using fs laser pulses with repetition rates of tens of MHz, we obtained cell fusion when only one fs laser pulse was applied. It is supposed that using of a single-shot laser pulse regime reduces the risk of undesirable heating of cells that may occur at high repetition rates. The highest cell fusion rate (88.9%) was achieved when single laser pulse with energy of 35 nJ was applied to initiate the fusion of the blastomeres. About 50% of the fused embryos in this case showed normal development for at least 3 days post fusion.

The developed technique of laser-based cell fusion was also applied to fuse cell bodies of two neurons of mollusc Limnaea stagnalis. Laser-mediated merging of the contents of two neurons was usually completed within ~5-7 minutes. It is believed that the laser-based technique of neuronal fusion has a great potential because it can significantly help in solving the problem of nerve damage repair.
3. Optical injection with femtosecond laser pulses

We also obtained some promising results on laser-based delivery of exogenous substances into living cells of different cell lines. In these experiments, the laser source used was a Ti:sapphire laser (wavelength 800 nm, pulse frequency 80 MHz, pulse duration 60 fs). We applied tightly focused femtosecond laser pulses to create a transient hole in the plasma membrane of the cells. Cultured mouse fibroblasts, human adipose-derived stem cells etc. were irradiated for tens of milliseconds with fs laser pulses with the energies of 2-4 nJ per pulse. In order to control the hole formation and estimate the viability of the exposed cells fluorescent dyes propidium iodide and Calcein AM were added into the OptiMEM medium containing the cells. Figure 2 demonstrates the process of membrane perforation with fs laser pulses. Small amount of propidium iodide dye diffuses through the created hole and fluoresces in red when exposed to green light. The exposed cell remains viable. The technique of laser assisted cell membrane perforation can be effectively used for not only injection of impermeable dyes but also for injection of nucleic acids. The nucleic acid injection called transfection is believed to be one of the most promising tools for human gene therapy of various diseases.

References
PHOTOCATALYTIC PROPERTIES OF DOPED TITANIUM DIOXIDE NANO PARTICLES WITH ABSORPTION IN VISIBLE SPECTRAL RANGE

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Photocatalytic activity of nitrogen-doped and undoped TiO2 nanoparticles is presented. Doping induced by annealing in NH3/N2 gas atmosphere causes expansion of the absorption band into visible spectral range. In contrast, Annealing in pure N2 atmosphere shows no doping. Photocatalytic properties of the powders are examined by three different methods: generation of radicals under UV and visible light irradiation, inhibition of proliferation of Staphylococcus aureus bacteria and degradation of methyl orange in aqueous solution. The results indicate that the correlation between pre-treatment conditions and photocatalytic performance depends on the photocatalytic processes and cannot be generalized.

Nowadays nanoparticles are extensively used in different areas of industry and in consumer products, with titanium dioxide (TiO2) being one of the most widely-spread. In such areas as sunscreens or purification of water, the aim is to use TiO2 ability to absorb sunlight for skin protection against excessive doses of solar radiation or for degradation of germs. Intrinsically, absorption band of the material irrespective to crystal form is located in the UV spectral range. In order to cover wider solar spectral range and extend absorption from UV to visible, doping is one of options to implement. Here we study how nitrogen-doping in gaseous atmosphere affects the particle photocatalytic performance. Titanium dioxide (Sigma-Aldrich, 20-nm anatase) powder was pre-treated with either N2 or 2% NH3 in N2 gas. Typically, 1 g of TiO2 powder was annealed in the gases at 350 ºC, 450 ºC and 600 ºC with a gas flow rate of 50mL/min for 4 hours. Figure 1 depicts size distribution and absorption spectra of treated particles.

Figure 1: Size distribution of TiO2 aggregates annealed in pure N2 and NH3/N2 mixture (left) and their absorption spectra (right).

Radical production by nanoparticles
Photoactivity of catalytic materials can be assessed by measuring amount of photogenerated free short-lived radicals by electron paramagnetic resonance (EPR) technique. This method allows for detection of microwave energy absorbed by unpaired electrons on outer orbitals of the formed radicals. With an appropriate choice of stable markers responsible for signal generation, the technique is an efficient tool even at room temperature.
Figure 2 illustrates photocatalytic activity of the N₂- and NH₃-pre-treated TiO₂ nanoparticles from the viewpoint of radical formation (averaged after 6 sets of measurements). Comparing the plots, two features are notable: (1) irradiation with combined UV and visible light distinctly causes more intensive production of radicals than only with visible light and without light; (2) the NH₃-annealed particles (substitutional N-doped) are radical-active also in the visible range, in contrast to N₂-treated particles (only interstitial N-doping).

**Photocatalytic action on Staphylococcus aureus**

*Based on our current results, S. aureus is quite resistant to blue light (404 nm, 70 mW/cm²). Consistent increase in exposure time from 5 to 30 min leads to a reduction in the number of colony forming units (CFU) number from 98 to 60%. When using pristine TiO₂ nanoparticles, the sensitivity of microorganisms to blue radiation increases as shown by reduced CFU values of 67 and 27% for light exposures from 5 to 30 min, respectively (Fig. 3). Approximately similar bactericidal efficiency is found for TiO₂ nanoparticles samples treated in N₂. After 30-min exposure, CFU numbers are 30% and 29%. Also, surprisingly, the nanoparticles treated with NH₃ are less effective (CFU of 47% and 46%) than those annealed in N₂/NH₃. However, this result fits well to studies of photocatalytic degradation of methyl orange by similar nanoparticle suspensions but under different irradiation conditions (not shown).*

Our experiments with organic dye and bacteria showed unexpected photocatalytic behavior. Despite the enhanced light absorption in N-doped (substitutional) TiO₂ powders, both dye degradation and antimicrobial activities were lower than with the samples having only surface-bound nitrogen species. On the other hand, EPR analysis of the formed radicals showed that substitutional N-doping enhances radical formation as it would be expected from the better optical absorption but it contradicts to our antibacterial and dye degradation experiments. Such inconsistency however, may be resolved by considering that the photocatalytic activity of various semiconducting nanoparticles depends on several factors, not entirely on the efficiency of optical absorption (electron-hole pair photogeneration) and subsequent radical formation.
THE PECULIARITIES OF PHOTOCHROMIC MATERIALS PROPERTIES RECEIVED BY POLYMER IMPREGNATION IN SUPERCRITICAL CARBON DIOXIDE

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We were shown that supercritical fluid (SCF) impregnation of polymers, which contained polar difenilol and halogen groups (polycarbonat, fluoroplast, polyvinylchloride) by spirocompounds led to conformational changes with the stabilization of coloured merocianin form of photochrome. We have shown early the effect of long-lived colored form B of spiroantroocsazine (SAO) molecules was formed by its matrix immobilization into polycarbonate. In this work we have shown that this effect was more general. The effect was found for number of spirocompounds, which were entered into polar polymer matrixes by SCF impregnation method. It was shown so that colored forms of spirocompounds impregnated in halogencontaining matrixes had intensive fluorescence.

Photochromic properties of indoline spirooxazine (ISO) molecules containing naphtho-, anthro- and phenantro-fragments (SNO, SAO and SPO, respectively), which were introduced into thermoplastic polymers: polyethylene, polycarbonate (PC), polyvinyl chloride (PVC), and copolymer of vinylidene fluoride with tetrafluorethylene (fluoroplast-42, F-42) in the supercritical carbon dioxide (SCCD) medium were investigated. Spirocompounds are the most important class of photochromic compounds, due to high efficiency of their phototransformations and significant photochemical stability. It is shown that the functional properties of the ISO introduced into the polymer using SCCD depend strongly on the chemical structure of the matrix and the nature of the ISO. Previously, it was found that the photochromic ISO can be effectively introduced by supercritical fluid (SCF) into thermoplastic polymers (polycarbonate, polymethyl methacrylate) and in the space-based cross-linked polymers on the base of substituted methacrylates, to the mass content of 8-10%.

It is shown that the SCF impregnation of PC, F-42, PVC by spirocompounds leads to conformational rearrangements in the ISO molecules with the stabilization of merocyanine (flat) forms of photochromes with different polarity. The form, in which contains the ISO in the polymer matrix depends on the nature of the polymer. In particular, all the PE ISO existed only in the original form A, ISO in PC - in the form of A (SNO, the SAO, the SPO) and in the form of B (SAO, SPO). All photochromes impregnated to the F-42 in the medium SCCD existed only in the first found Bx form, with a maximum absorption band shifted to the violet region of 70-100 nm compared with the absorption of the B form. In PVC the form A and the two colored forms, B and Bx, are fixed for all ISO. The maximum number of ISO introduced into the polymer using SCF-impregnation was depended on the ISO molecular size and the physical state of the polymer. In particular, the degree of impregnation of polymers, for which the temperature of the SCF treatment (900°C) higher than the glass transition temperature Tg (F-42 and PVC), was higher than the degree of impregnation for the PC, with Tg ~ 1500°C. The number of the spirooxazines entered to the PC in the same conditions increased in number [SNO] ~ [SPO] ~ [SNO], and the size of the molecules ISO decreased in the same sequence. It is shown that the forms B and Bx in the PC, F-42 and PVC treated in the SCCD were stable under normal conditions and under thermal and photo-processing. Such stabilization of the ISO form in the PC, F-42 and PVC could be associated with the formation of intermolecular donor-acceptor complexes of fragments of the form of ISO with the bis-phenilol groups of PC, or halogen groups of the PVC and F-42 macromolecules. The formation of stable complexes becomes possible due to swelling of the polymer in the SCF, which facilitates the process of introducing the ISO into the polymer matrix and the isolation of the ISO in the polymer that prevents the return of the ISO in the initial nonplanar form A after complete removal of the solvent (CO2).

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References
Yb-doped laser materials for high-power sub-100 femtosecond thin disk lasers

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Ultrafast thin disk lasers, passively modelocked with semiconductor saturable absorber mirrors (SESAMs), currently achieve the highest average powers and pulse energies compared to any other ultrafast laser oscillators. To date an average power of >140 W and a pulse energy of >40 µJ have been demonstrated [1]. However, until now the pulse duration has been too long for efficiently driving high harmonic generation (HHG). Here we present the progress for scaling the pulse duration into the sub-100 femtosecond domain. The two key elements to reach such a performance are firstly the disk gain material and second the SESAM. The gain material has to have a short absorption length, high thermal conductivity and a large gain bandwidth that supports femtosecond pulses. Two important requirements on the SESAM are a reduced two-photon absorption and a large damage threshold [2]. A group of very promising disk materials are the Yb-doped sesquioxides among which we find Yb:Lu2O3 and Yb:LuScO3. With Yb:LuScO3 we obtained for the first time thin disk laser performances in the sub-100-fs regime, opening the door to new research in extreme nonlinear optics such as intralaser HHG and VUV/XUV spectroscopy.

1. Introduction
To date passively modelocked thin disk lasers (TDLs) [3] using SESEmiconductor Saturable Absorber Mirrors (SESAMs) [4] enable the highest average powers and pulse energies of any femtosecond oscillator technology. The thin gain medium of only a few 100 µm allows for efficient heat removal and provides excellent linear and nonlinear optical properties. In principle, the output power of modelocked TDLs can be scaled up by increasing the beam diameters on both the thin disk gain medium and the SESAM, without detrimental nonlinear effects.

Figure 1: Overview of average power of modelocked TDLs versus pulse duration. Using the sesquioxide Yb:Lu2O3 we managed to decrease the pulse lengths further down to 142 fs by exploiting >70% of the gain spectra of this thin disk material. Even shorter pulses were achieved from an Yb:LuScO3 TDL, where we entered the sub-100-fs regime.

2. Generation of short pulses
TDLs are power scalable, thus they are excellent candidates for an important number of scientific applications, such as high harmonic generation for compact VUV/XUV sources, that require energetic femtosecond pulses from table-top sources operating at megahertz repetition rates [5, 6]. However, short pulses (< 200 fs) are required to drive these experiments efficiently. Obtaining shorter pulses from high power TDLs is a topic of extensive investigation (Fig. 1) that yields some demands on the disk material that will be discussed in the next section.

2.1 Promising gain materials
The first modelocked TDL was based on a Yb:YAG disk [7], which today is the most widely-used gain material for TDLs. Because of its good thermal conductivity of 7 Wm⁻¹K⁻¹ for an Yb³⁺ doping concentration of 3 at.%, this material is a good candidate for operation at high output power. Even though Kerr-lens modelocked Yb:YAG thin disk oscillators demonstrated 200 fs short pulses [8], typical pulse durations of SESAM modelocked Yb:YAG TDLs have been limited to about 700 fs. Thus other thin disk materials have to be considered as candidates for the generation of short pulses.

The borate material Yb:YCa₄O(BO₃)₃ (Yb:YCOB) shows a promising gain bandwidth for the generation of short pulses. Modelocking experiments with the Yb:YCOB resulted in a pulse length of 227 fs at 2 W [9]. The disadvantage
of this material is its low thermal conductivity, which is about 5 times smaller than for Yb:YAG, what makes a further increase in average output power a challenging task.

Another successful thin disk material group are the Yb-doped cubic sesquioxides. Among these materials we find Yb:Lu₂O₃ (Yb:LuO), that has a higher thermal conductivity than Yb:YAG and that is therefore a good candidate for results with highest average output power. The highest average output power of 141 W in 738 fs we obtained out of an Yb:LuO thin disk laser [10] has been surpassed only by an Yb:YAG thin disk oscillator build by Bauer et al., delivering 145W of average output power and 1.1 ps pulses [1]. Compared to Yb:YAG, Yb:LuO has an emission spectra that is twice as broad and is therefore not only an interesting gain material for power scaling but also for short pulse generation. In a recent experiment we obtained pulses as short as 142 fs at an average output power of 7 W [11]. With a modelocked optical spectrum of 8.5 nm fullwidth half maximum (FWHM) we used more than 70% of the available FWHM emission bandwidth of Yb:LuO.

The combination of the two emission spectra of Yb:LuO and Yb:ScO₃ results in the mixed sesquioxide Yb:LuScO₃ (Yb:LuScO) [12]. This gain material has a broad emission bandwidth of 22 nm (Fig. 2). TDLs based on Yb:LuScO as gain material achieved performances in the sub-300-fs regime with average output powers of up to 23 W [2]. During the last year we have managed to decrease the pulse duration to 96 fs at an average output power of 5.1 W [13]. This was the first demonstration of a SESAM modelocked TDLs delivering pulse lengths below 100fs.

![Figure 2: Gain spectra of the three sesquioxides Yb:Lu₂O₃, Yb:Sc₂O₃ and Yb:LuScO₃ (the stoichiometric mixture of the first two). The 22 nm broad emission bandwidth of Yb:LuScO₃ is centered around 1038 nm and delivered the first sub-100 fs pulses at an average output power of 5.1 W.](image)

### 3. Conclusion and Outlook

We discuss the potential of different thin disk gain materials for shorter pulse generation. Pulses as short as 142 fs were obtained with the sesquioxide material Yb:Lu₂O₃, which has already demonstrated its suitability for high power operation in the thin disk geometry. Further improvements in SESAM design [2] and enlarging the mode size on the gain material will enable us to reach the same pulse lengths at higher power levels in comfortable cavity conditions. Mixing the two sesquioxides materials Yb:Lu₂O₃ and Yb:Sc₂O₃ results in the very broadband gain material Yb:LuScO₃ that allowed for the first time a SESAM modelocked TDL operation in the sub-100 fs regime with an average output power of 5.1 W. Although the obtained output power is still moderate, the intracavity power was >200 W and thus this result is an interesting starting point for scientific applications in extreme nonlinear optics applying intralaser HHG.

### References


OPTICAL PROPERTIES OF POLY(METHYLMETHACRYLIMIDE) DOPED WITH BISMUTH IONS

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We report about the optical properties of bismuth doped poly(methylmethacrylimide) layers and bismuth doped poly(methylmethacrylimide) layers co-doped with ytterbium ions. Photoluminescence spectra around 1300 nm were observed and co-doping with ytterbium ions had positive effect on the 1300 nm luminescence. Optical properties of the samples were evaluated on the bases of the concentration of the bismuth ions as well as that of the co-doping with ytterbium ions and showed, e.g., close relations between concentration of the dopants and intensity of the luminescence band around at 1300 nm.

1. Introduction

Optical materials doped with active ions are intensively studied during the past decades due to increasing demand for optical sources and amplifiers operating at wavelengths compatible with fiber communications systems. Long-haul optical communication systems using silica fiber use two bands around at 1300 and 1550 nm, which coincide with two silica fiber low optical loss windows: one between 1200 to 1350 nm and the second one from 1450 to 1600 nm. The most commonly used optical amplifiers for operating at 1550 nm are those made of Erbium Doped Fiber Amplifier (EDFA) [1]. These amplifiers exhibit unique characteristic due to the intra-4f \( {^1}I_{13/2} \rightarrow {^1}I_{15/2} \) transition of erbium (Er\(^{3+}\)) ion, which corresponds to 1535 nm emission. Optical materials doped with neodymium (Nd\(^{3+}\)) and praseodymium (Pr\(^{3+}\)) ions have been proposed for amplification from optical amplifiers operating at 1300 nm [2, 3]. But Pr\(^{3+}\) amplifiers have small low-quantum efficiency and higher noise. The majority of the world optical communication system operates in this wavelength and there is strong need for an efficient optical amplifier in this region. Therefore new gain medium to cover not only bend 1200-1300 nm but also bend 1450-1600 nm is strongly required.

Recently, Fujimoto and Nakatsuka presented that this new dopant for infrared luminescent can be bismuth (Bi\(^{3+}\)) ions [4, 5]. It was also shown that Bi\(^{3+}\)-doped optical materials have many attractive features, which make them suitable for the optical amplifiers and sources operating not only for band around 1300 nm but at hole near-infrared spectral regions from 1000 to 1600 nm [6]. Nowadays, a possibility of enhancing the near infrared emission of the optical materials by co-doping them with transition metal ions is also investigated. The most often used sensitizer is ytterbium (Yb\(^{3+}\)) ions. It was previously shown that not only Er\(^{3+}\) doped optical material co-doped with Yb\(^{3+}\) have higher photoluminesence efficiency [7] but it was also presented that Bi\(^{3+}\) doped optical materials co-doping with Yb\(^{3+}\) ions have higher optical gain and wider width of the transmitted bandwidth [8, 9]. The development of new photonics materials such as polymers rapidly increased. Therefore we are going to investigated properties of polymer layers doped with Bi\(^{3+}\) and Bi\(^{3+}/\)Yb\(^{3+}\) ions.

2. Experimental and Results

In this paper we report about the optical properties of Bi\(^{3+}\) ions doped poly(methylmethacrylimide) (PMMI) layers and about properties Bi\(^{3+}\) doped PMMI layers co-doped with Yb\(^{3+}\) ions. The Bi\(^{3+}\) doped PMMI layers supported by Evonik R. h m GmbH and containing bismuth were fabricated by spin-coating onto silicon substrate or the polymer was poured into a bottomless mold placed on a quartz substrate and let to dry in air. Bismuth chloride (BiCl\(_3\)) was dissolved in dimethylsulfoxide (C\(_2\)H\(_6\)OS) (Sigma-Aldrich), so that the concentration of bismuth in the solutions ranged from 1.0 to 20.0 at. %. The co-doping with Yb\(^{3+}\) transition metal ions was performed by the same way as the Bi\(^{3+}\) doping, i.e., adding the ytterbium chloride (YbCl\(_3\)) of the pertinent metal dissolved in the aforementioned solvents into the Bi\(^{3+}\) doped PMMI precursor and depositing the layers by the procedure described above.

The properties of the material were studied using several methods with special regards to its potential utilization in photonics devices. Transmission measurements were performed using a UV-VIS-NIR Spectrometer (UV-3600 Shimadzu) in the range from 300 to 1600 nm. We observed that the transmission spectra of the Bi-doped PMMI polymer increasing level of the doping shifted the transmission edge to the longer wavelengths. Similar dependence appeared also at Bi\(^{3+}\) doped PMMI co-doped with Yb\(^{3+}\) ions.

The infrared spectra were characterized by using infrared spectroscopy using the Bruker IFS 66/v FTIR spectrometer and we investigated presence of OH impurities which can be cause by the chloride hygroscopic precursors. These investigation was done due to that presence of water may be a serious obstacle in obtaining a good function of the actual realized device.

Laser LD808 with excitation wavelength 808 nm (250 mW, room temperature) was used to measure photoluminescence spectra (PL) in the range from 1100 to 1500 nm. Figure 1a gives obtained PL spectra of PMMI layers doped with
different amount of Bi\(^{3+}\) ions and Figure 1b shows PL spectra for PMMI layers doped with Bi\(^{3+}\) ions (1.0 at.\%) and co-doped with different amount Yb\(^{3+}\) ions (from 1.0 to 20.0 at.\%).

Fig. 1a shows photoluminescence band around 1270 nm caused by Bi\(^{3+}\) ions transition and the intensity of the bands increase with increasing concentration of Bi\(^{3+}\) in the samples. Maximum PL intensity was observed for samples with maximum Bi\(^{3+}\) content (20.0 at.\%). Fig. 1b shows that intensity of the bands increase with increasing concentration Yb\(^{3+}\) co-doping. The strongest PL intensity at 1270 nm wavelength was observed in the samples containing 15 at.\% of Yb\(^{3+}\) ions and we observed that the samples with higher concentration of Yb\(^{3+}\) ions PL intensity do not increase. Therefore we suppose that feature can be attributed to the so called “concentration quenching effect,” which is a well-known phenomenon, e.g., for the Er\(^{3+}\) doped materials (see, e.g. 1). It was found that this effect has a close connection not only with the higher concentration of the dopants but also with chemical composition and structure of the hosting material.

3. Conclusion

We report about optical properties of the poly(methylmethacrylimide) doped with bismuth ions and co-doped with ytterbium ions. Optical properties were evaluated on the bases of the concentration of the bismuth ions involved in the samples and showed, e.g. close relations between concentration of the dopants and intensity of the luminescence band at 1300 nm. Transmission spectra showed that the Bi\(^{3+}\)-doped PMMI polymer increasing level of the doping shifted the transmission edge to the longer wavelengths. IR spectra showed only negligible changes in the original PMMI layers. The emission around 1300 nm was observed in the doped polymer layers under 808 nm laser excitation and the co-doping with Yb\(^{3+}\) ions increased PL intensity. Increasing concentration of the Yb\(^{3+}\) ions has also positive influence on the full width at half maximum. PL intensity with the sample containing 20.0 at.\% of Yb\(^{3+}\) indicating thus possibility of concentration quenching effect. The results of our research proved that the doping Bi\(^{3+}\) ions has a strong potential for application in active photonics structures, as it has excellent optical properties and very easy and not demanding fabrication procedures.

References


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Millijoule Energy Passively Q-Switched Diode-Pumped Tm-doped Fluoride Lasers

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Abstract: Passive Q-switching of Tm-doped fluoride lasers including Tm:LiYF4 and Tm:LiLuF4 is demonstrated for the first time, using polycrystalline Cr2+:ZnS as a saturable absorber. The pulse energies are at the millijoule level and the peak powers at the 100-kW level, which represent an improvement of more than an order of magnitude for diode-pumped Tm-lasers operating at ~1.9 μm. Simultaneously, the pulse duration of 7.6 ns achieved represents the shortest pulses obtained so far from a Q-switched Tm-laser. The LiLuF4 host with higher Tm-doping and enhanced cross-relaxation effect shows superior performance.

1. Introduction

The Tm3+-ion emission originating from the 3H4 → 3F4 transition is located in the eye-safe spectral region and has potential applications in the fields of laser, radar atmosphere monitoring and military technologies. Continuous-wave (cw) powers exceeding 100 W have been already demonstrated under diode pumping near 800 nm [1]. Short pulse Tm-lasers at ~1.9 μm are interesting for pumping Optical Parametric Oscillators (OPO’s) which can efficiently convert radiation to the mid-IR spectral range because the most promising nonlinear materials, ZnGeP2 and orientation-patterned GaAs exhibit residual or two-photon absorption at shorter wavelengths. Fluoride crystals exhibit low phonon energy and long fluorescence (energy storage) times [2] which is beneficial for generating high energies and peak powers in Q-switched operation. Passive Q-switching (PQS) is much simpler and cheaper for realization than active Q-switching and more important, shorter pulses are generated with higher peak power which is advantageous for OPO pumping. It has been applied to several Tm-doped laser materials such as KY(WO4)2, KLu(WO4)2, YAG, and YAP, using Cr2+ (Cr)-doped ZnSe and ZnS crystals, PbS quantum dots, and InGaAs/GaAs semiconductor based saturable absorbers (SAs). Here, we report results obtained with two fluoride crystals, Tm3+:LiYF4 (Tm:YLF) and Tm3+:LiLuF4 (Tm:LLF), under cw diode pumping using ceramic Cr:ZnS SAs. In the LLF isomorph of YLF, Y ions are replaced by Lu and improved laser performance could be expected with Tm-doping due to the closer ionic radii of Tm and Lu [2]. Compared with Tm:YLF, Tm:LLF crystals exhibit better optical quality related to the congruent melting character and improved thermo-mechanical properties.

2. Experiments and results

The pump source employed was a fiber-coupled, NA=0.22, 200 μm core diameter AlGaAs laser diode operating at ~802 nm. The pump beam was delivered onto the Tm laser crystals through a plane input coupler highly reflective (HR) for the laser wavelength. A 45° plane bending mirror, HR for the laser wavelength, transmitted the residual pump radiation while the SA was positioned between this mirror and the 10 cm radius of curvature output coupler forming a hemispherical cavity. The output coupler had a transmission minimum of ~32% at 1930 nm.

The a-cut 12% Tm:LLF and 8% Tm:YLF samples were 3.54- and 3-mm thick, respectively, used at normal incidence. The 2.2-mm thick Cr:ZnS SAs were specified with low signal transmission (corrected for Fresnel reflections) of T0= 78 and 85% at 1910 nm. Their AR-coating reduced the reflection to ~1% per surface and the SAs were used also at normal incidence.

For Tm:YLF with the T0=85% SA, the pulse energy was almost independent of the repetition rate, around 850 μJ. The repetition rate increased from 39 to 120 Hz with the pump power (Fig. 1a). The maximum average power was 98 mW. The pulse duration remained almost constant with pump power, around 14 ns. The highest pulse energy obtained, ~900 μJ (Fig. 1a), corresponds to ~65 kW of peak power. For Tm:LLF, the maximum pulse energy with this SA was 1.14 mJ (Fig. 1b). At a repetition rate of 203 mW and 16.4 ns. The highest peak power was again ~65 kW.

With the T0 = 78% SA, the Tm:YLF laser was very inefficient. For Tm:LLF, however, the maximum single pulse energy reached 1.26 mJ (Fig. 2). At a repetition rate of 161 Hz this produced an average output power of 203 mW (Fig. 2). With a pulse width of 7.6 ns this gives a record peak power of 166 kW for a PQS Tm-laser. The pulse train stability was ±12% at maximum output power. The output coupler had a transmission minimum of ~32% at 1930 nm.

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The Tm:YLF laser was naturally π-polarized oscillating at 1886-1887 nm. The Tm:LLF laser output at 1891 nm was also naturally π-polarized. This can be explained by the higher gain cross sections for polarization parallel to the c-axis at the given inversion rates. The latter are determined by the actual output coupler transmission which was ~50% and ~45% at the corresponding wavelengths.

3. Conclusion

In conclusion, efficient PQS operation of diode-pumped Tm-lasers at ~1.9 µm has been achieved with Tm:YLF and Tm:LLF crystals. Fluoride crystals are very promising Tm-hosts for this regime. Using polycrystalline Cr:ZnS SAs, pulse energies at the millijoule level and peak powers at the 100 kW level have been achieved which represents an improvement of more than order of magnitude for diode-pumped Tm-lasers operating at ~1.9 µm. Also, the pulse duration of 7.6 ns achieved represents the shortest pulses obtained from a Q-switched Tm-laser. The LLF host with 12% Tm-doping and enhanced cross-relaxation effect showed superior performance.

References

Emission and laser properties of Bi/Si co-doped silica-based glasses and fibers

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The emission and laser properties of Bi/Si co-doped silica-based glasses and fiber have been investigated in this work. The effects of Si doping on the near infrared (NIR) luminescence were observed in low concentration Bi doped (0.1mol%) glasses. The broadband NIR emission can only be observed when Si is introduced in Bi-doped glasses, the optimal Si concentration of ~0.1mol% can enhance the emission intensity of Bi-doped glass in this experiment. The origin of fluorescence can be attributed to Bi ions at low valence due to the reduced property of Si. The Si/Bi co-doped fiber was fabricated by MCVD and solution doping method. Under 980nm LD pumping, the laser operation with the peak wavelength about 1150nm was observed.

1. Introductions
Bismuth-doped glasses and fiber have attracted growing attention in recent years because of their applications including broadband fiber amplifier, tunable fiber laser, and supercontinuum operation [1-4]. Broadband emission in the range of 1100-1500nm have been observed in Bi-doped aluminosilicate, borate, phosphate, germanate glasses and chalcogenide glasses[5,6]. Numerous investigations are focused on Bi-doped silica-based glasses and fiber due to its excellent physical, chemical, thermal properties and compatibility with conventional silica fiber, furthermore the Bi-doped silica fiber is perfect material for high energy laser output because of its higher laser breakdown threshold than other glasses matrix. In recent years, various Bi-doped silica fiber have been fabricated, and the ~50% laser efficiency has been achieved near 1200nm with the Bi-doped silica fibers. Although the mechanism of Bi emission has been not clear until now, it is helpful for emission enhancement and laser operation to promote the formation of bismuth emission center in glasses or fibers. In this work, the introduction of Si can enhance the absorption and emission intensity efficiently in low Bi concentration (~0.1 mol%) doped silicate glasses. The laser operation with the peak wavelength about 1150nm was observed with Bi/Si codoped silica fiber fabricated MCVD and solution doping method.

2. Experimental
Glass samples with compositions 65SiO2-10Al2O3-25CaO-0.1Bi2O3-xSi (Si=0, 0.03, 0.05, 0.1, 0.2mol% respectively) were prepared by a conventional melting method. Analytical pure reagent commercial oxides (>99.5%) were selected as the raw materials. Si powder was introduced into the raw material as reducing agent. The mixed batch of 30g were melted in alumina crucible at 1580°C for 2 hours in reducing atmosphere achieved by the introduction of Si powder. The glass melts were poured on the pre-heated steel mold and then annealed near the glass transition temperature for 2hrs in the annealing furnace. The obtained glasses were cut into 15×15 ×2 mm3 and polished for optical measurement. Optical absorption spectroscopic was measured on PerkinElmer-Lambda35 spectrophotometer in the range of 200-1100 nm. The luminescence spectra were obtain by ZOLIX SBP300 spectrophotometer, detected by InGaAs photo-detector with excitation 808 nm LD. The Si/Bi doped fiber is fabricated with MCVD method, the nano particle of Si (~10-30nm) is introduced by solution method. The laser output operation is measured under 980nm LD pumping.

3. Results and discussion

3.1 Absorption and emission of Si/Bi codoped glasses
Figure 1 shows the absorption spectra of SiO2-Al2O3-CaO-Bi2O3 (SACB) co-doped with various Si concentration, absorption intensity enhancement are observed obviously with the increase Si concentration. Fig.2 shows the emission spectra under 808nm excitation, NIR luminescence can not be observed from single Si doped silicate glass without bismuth (sample SAC-Si) neither, which is suggested that near-IR fluorescence centered at 1300 nm is derived from Bi ions rather than Si, and Si played a supporting role only for the near-IR emission of Bi.
3.2 Laser operation of Si/Bi codoped fiber

The laser operation of 5m Si/Bi codoped fiber is observed under 980 nm LD pumping, which is shown in Fig.3. The laser wavelength is about 1150nm. The mismatch of dichroic mirror probably lead to the presence of fluorescence from 1170 nm to 1300 nm.

3.3 The effect of Si on the luminescence center formation of Bi in glass

The introduction of Si contributes to the enhancement of absorption and emission intensity. The reducing condition introduced by Si powder promotes the formation of Bi active centers in Bi doped glass and emitting superior NIR luminescence. Reaction formula of this phenomenon in the melting process can be expressed as:

$$2Bi_2O_3 + 3Si \rightarrow 3SiO_2 + 4Bi_{\text{active-center}}$$

References


B-TYPE DELAYED FLUORESCENCES OF DBA MONOMERS AND DIMERS

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Highly sensitive detection of singlet-singlet, triplet-triplet optical absorptions and delayed fluorescence of 1,2:5,6-dibenzanthracene(DBA) in polymethylmethacrylate (PMMA) were experimentally observed by flash and laser flash photolysis techniques. 1,2:5,6-dibenzanthracene molecules were excited in a two-step process. In the first step the excited singlets are created by optical pumping, which undergoes intersystem crossing to triplet state, then triplet-triplet absorption creates an excited triplet 1,2:5,6-dibenzanthracene molecule which returns to the first excited singlet level by intersystem crossing. The re-created first excited singlets of monomers and dimers of 1,2:5,6-dibenzanthracene decays back to the ground state by emitting B-type of delayed fluorescences of monomers and dimers, which were observed at the same emission bands of normal fluorescence of monomers and dimers.
We have investigated polarization and angular dependences of the luminescence intensity of Stark transitions in Nd:YVO₄, Nd:GdVO₄, and mixed Nd:YₓGd₁₋ₓVO₄, Nd:YₓSc₁₋ₓVO₄ vanadate crystals. Using angular dependences of the luminescence intensity of Stark transitions in vanadate crystals we can create active medias with different coefficients of gain and wavelengths. The high peak power UV-VIS-IR passively Q-switched (Cr⁴⁺:YAG saturable absorber) laser based on variable-cut Nd:GdVO₄ vanadate crystals was realized for medicine applications.

One interesting application in biology and medicine is the action of low-intensity UV radiation on various microorganisms. Medical treatment of patients suffering from fibrous-cavernous pulmonary tuberculosis is still difficult and urgent problem in modern medicine. Further experiments with laser radiation at the wavelength 266 nm show higher efficiency of the action of this radiation on microorganisms. Thus, it seems reasonable to create low-cost and simple UV laser medicine systems for further development of the treatment of patients suffering from tuberculosis and other diseases.

We present UV laser sources based on a novel methods control of spectral parameters in diode-pumped vanadate lasers. Spectroscopic and lasing properties of Nd:YVO₄, Nd:GdVO₄ and mixed Nd:YₓGd₁₋ₓVO₄, Nd:YₓSc₁₋ₓVO₄ crystals were investigated. We have investigated polarization and angular dependences of the luminescence intensity of Stark transitions in vanadate crystals. The frequency shift and redistribution of the luminescence intensity of Stark transitions are observed.

It is known, that too large emission cross-section of with a-cut π-polarized vanadate crystals is a shortcoming for Q-switched lasers, because it limits their energy-storage capacity, leading to smaller pulse energies. Usial methods to avoid this drawback are to use c-cut crystals, a-cut σ-polarized radiation or mixed vanadate. However wavelengths of c-cut and a-cut σ-polarized vanadate crystals distinct from a-cut π-polarized emission. In addition c-cut vanadate crystals have nonpolarised radiation.

Using angular dependences of the luminescence intensity of Stark transitions in vanadate crystals we can create active medias with different coefficients of gain and wavelengths.

Laser operation under different angles of cut were investigated for Nd:GdVO₄. Variable-cut vanadate crystals have the polarized radiation, and wavelengths of radiation coincide with a-cut π-polarized emission. It allows creating effective master oscillator-amplifier systems. Cr⁴⁺:YAG saturable absorber with initial transmission 82 % and 75 % oriented with their normal along the (111)-crystal axis, were used as the passive Q switch.

We have shown experimentally that the variable-cut Nd:GdVO₄ laser could have good passively Q-switched performance, which gives the narrowest pulse of 1.5 ns with the highest peak power of 21 kW. In addition the vanadate crystals have the polarized radiation. High peak power and beam quality of the IR lasers are required for efficient conversion of the radiation into visible or UV spectrum range by means of nonlinear crystals. The average power of visible and UV radiation up to 310 and 7 mW has been obtained in the case of extracavity conversion of the laser radiation in crystals KTP and BBO, respectively.

We have demonstrated a low-cost, compact, high-efficiency passively Q-switched UV-VIS-IR laser medicine systems based on the variable-cut Nd:GdVO₄ laser with Cr⁴⁺:YAG saturable absorber crystal.
Kerr-lens mode locking in a ring bidirectional YAG:Cr$^{4+}$ laser

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In this work we investigated how the spectral characteristics of laser transition of the broadband active medium affect the level of fluctuations and stability of bidirectional generation, and stability of mode locking in a ring laser in the rotation sensing mode. We developed the model of bidirectional generation of such a laser taking into account spectral properties of the active medium. In order to find the polarization of the laser crystal we used the quantum kinetic equations for density matrix. Experiments in our setup revealed that generation of the laser had a cluster character. Luminescence spectrum of the YAG:Cr$^{4+}$ crystal and generation spectra of the laser showed that this medium has both homogeneous and inhomogeneous broadenings. Stable bidirectional generation is a result of the fact that competition between counterpropagating waves is less than in the case of homogeneously broadened medium.

Kerr-lens mode-locked lasers with broadband active media (Al$_2$O$_3$:Ti$^{3+}$, Mg$_2$SiO$_4$:Cr$^{4+}$, YAG:Cr$^{4+}$) are usually used as sources of femtosecond pulses with tunable frequencies. Laser gyroscopes with such active media have a large potential due to their fabricability, generation effectiveness, mechanical reliability and high accuracy. The majority of solid-state active media has homogeneous broadening of laser transition that results in a strong competition between counterpropagating waves and complexity of generation dynamics [1-3] in ring lasers with such active media. But in ring lasers with broadband active media Kerr-lens mode locking with femtosecond pulse generation can be achieved, and the wave competition and lock-in effect can be reduced essentially. This indicates that lasers with broadband active media have good prospects in laser gyroscopy.

We created an experimental setup based on the ring YAG:Cr$^{4+}$ laser (fig.1) [3]. This active medium was chosen because of several reasons. YAG:Cr$^{4+}$ has good thermal and mechanical properties. To pump the laser it is convenient to use a laser diode or a fiber laser with wavelength $\sim 1\mu$m. Due to the broad amplification line (1340-1580 nm) including the area of low loss in the optic fiber ($\sim 1.5\mu$m) 20 fs pulses can be generated in the laser.

Ring laser used as a laser gyro must have stable bidirectional generation and (in the case when mode locking is used to reduce the lock-in zone) stable mode locking regime. To improve the stability and to reduce the level of fluctuations of the laser it is necessary to carry out the calculations with taking into consideration the spectral characteristics of the laser transition and the broad amplification line. To model the bidirectional generation in a ring laser we used the semiclassical self-consistent approach [1,2,5]. Field in the cavity is determined from the wave equation and can be represented as a superposition of fields of counterpropagating waves that can be expanded into longitudinal modes [1-3]. In order to find the polarization we solved the material equations for evolution of density matrix of solid-state broadband medium. The polarization of the medium with both homogeneous and inhomogeneous broadenings is a sum of the contributions of different groups of centers. We represent the spectrum of our active medium as a sum of contributions of several groups of homogeneously broadened centers. The elements of density matrix can be determined from the quantum kinetic equations [1,2] in two level approximation with taking into account the pump, relaxation transitions between the levels and the relaxation of the off-diagonal elements of the density matrix.

The results of the simulation were tested in the experimental setup including the ring YAG:Cr$^{4+}$ laser pumped by ytterbium fiber laser. We obtained the stable bidirectional generation (fig.2). Experiments in our setup revealed that generation of the laser had a cluster character. Luminescence spectrum of the YAG:Cr$^{4+}$ crystal and generation spectra

![Fig.1. Optical scheme of the ring laser.](image-url)
of the laser showed that this medium has both homogeneous and inhomogeneous broadenings. This fact can lead to reduction of the competition between counterpropagating waves in the ring laser. Laser generation (chopped spectral line on the fig. 3) slightly reduces the level of the luminescence only at high-frequency part of the luminescence spectrum and has no effect on the level of the luminescence at the frequencies neighbour to the operating frequency (fig. 3). Therefore laser generation does not reduce the amplification at the frequencies neighbour to the operating frequency.

Our investigations show that because of spectral characteristics of broadband active medium the competition between counterpropagating waves in the ring YAG:Cr$^{4+}$ laser is small so the ring laser with this active medium has prospects for application as a laser gyroscope.

References
A Study on the Vibration Characteristics of CFRP Composite Materials by using Time-Average ESPI

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Abstract

The ESPI (Electronic Speckle Pattern Interferometry) is a real-time, full-field, non-destructive optical measurement technique. In this study, ESPI was proposed for the purpose of vibration analysis for new and composite materials. Composite materials have various complicated characteristics according to the materials, orientations, and the stacking sequences of the ply and boundary conditions. Therefore, it is difficult to analyze composite materials. For efficient use of composite materials in engineering applications the dynamic behavior (i.e., natural frequencies and nodal patterns) should be known. With the use of Time-Average ESPI, one could easily analyze vibration characteristics of composite material by real time. We manufactured two kinds of laminated composites (i.e., symmetry and asymmetry) which were composed of CFRP (Carbon Fiber Reinforced Plastics) and the shape of the test piece was of rectangular form.

1. Instruction

The Noise and vibration problems during the operation of vehicle engines and machine tools are one of the most important issues to machine designers (Suzuki, 1989; Sakada, 1979). To find the practical aspect of these problems, we have measured the vibration modes of rectangular plates clamped at two parallel edges by ESPI (Cloud, 1995; Ennos, 1975; Jones and Wykes, 1989). ESPI (Electronic Speckle Pattern Interferometry) (Kang and Moon, 1996; Kim and Yang, 1994; Kim et al., 1998), which was developed by adding the television image acquisition and the computer image processing to SPI, is a new method for the analysis of the vibration problems (Kang and Choi, 1996; Rastogi, 1997; Sirohi, 1993). In this paper, vibration modes are measured for laminated composite materials (Symmetry, Asymmetry). Frequencies obtained from the measurement are qualitatively compared with those of the theoretical analysis proposed by Warburton who considered the vibration of rectangular plates with all possible boundary conditions (Warburton, 1954).

2. Experimental Setup

We manufactured laminated composite materials of symmetry and asymmetry configurations, which consisted of CFRP (Carbon Fiber Reinforced Plastics) and the shape of the specimen was of rectangular form. We used a laminated plate of fabric form that was not a laminated plate in uni-direction. The laminated composite material specimen had a thickness of 3mm and a size of 200mm by 150mm. Figure 1 shows the two kinds of CFRP: (a) symmetry laminated plate [0°/90°/45°/-45°]2s and (b) asymmetry laminated plate [45°/-45°/90°/0°]2T. A photographic image of the Time-Average ESPI system to measure vibration mode is shown in Fig. 2.

Fig. 1 (a) symmetry laminated plate, (b) asymmetry laminated plate

Fig. 2 Time-Average ESPI system setting
3. Experimental Result

Each of the vibration fringe patterns of symmetry and asymmetry laminated composite materials are shown Fig. 6 and 7. The fringe patterns were of different form with uni-direction composite materials than those that were studied previously. The fringe patterns of symmetry laminated composite materials were clearer than the asymmetry laminated composite materials.

![Fig. 3 Vibration fringe patterns of symmetry laminated composite materials](image1)

![Fig. 4 Vibration fringe patterns of asymmetry laminated composite materials](image2)

4. Conclusion

This system could measure the vibration mode of laminated plates in fabric form. Also, it could be used to evaluate the practical application of the Time-Average ESPI system on manufactured symmetry and asymmetry laminated composite materials, as well as the vibration modes on these materials. The fringe patterns of symmetry laminated composite materials were clearer than those of the asymmetry laminated composite materials. The shape of the vibration mode was more unstable in asymmetry laminated composite material. This Time-Average ESPI system could measure vibration mode and natural frequency without being influenced with the state of interior as well as external forms and the quality of the material. When we observe the vibration mode using FEM(Finite Element Method), we must first know the properties, as well as the state and the condition of the composite materials. But, if we use the Time-Average ESPI system in this study, we don't need to know the properties, the state and the condition of composite materials and we could observe the vibration mode by real time in an easier and faster way.

References

SUPERCONTINUUM GENERATION OVER 2 µm.

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Effective supercontinuum generation in fiber media in spectral range over 2 µm was experimentally demonstrated. Supercontinuum generation was observed in passive germanium doped fiber with maximum wavelength near 2.7 µm. Supercontinuum generation was obtained in holmium optical fiber amplifiers medium with spectral density 10 W/nm. In thulium fiber amplifiers observed amplification not only in conventional range near 1.8 µm, but in spectral range from 2.3 to 2.5 µm, that corresponds to ³H₄→³H₅ optical transition possibility in thulium-doped optical fibers.

1. Introduction
Supercontinuum generation beyond 2 µm is interesting due to the potential application in spectroscopy, atmospheric analysis, medicine, etc. As a rule, to generate supercontinuum in this spectral range special fibers are applied. For example, in [1] sapphire fiber was used, in [2,3] – microstructured fiber based on oxide glass with complex composition. Generation up to 4.8 µm was obtained in ZBLAN fiber [4]. The main disadvantage of such sources is the bad compatibility with standard communication fiber technology.

2. Experimental setup
2.1 Pump source.
Cladding pumped Q-switched Er-doped fiber laser was used as the pump source [5]. Q-switching was realized by emplacement of a self-saturable absorber based on a Tm-doped fiber. Lasing wavelength was of 1.59 µm, maximum output power was near 1 W with repetition rate of 4.4 kHz and pulse duration of 35 ns. Pulse energy of 0.21 mJ and peak power of 6 kW can be estimated.

2.2 Passive media.
We have tested 3 specimens of the heavily Ge-doped fiber with different lengths. All samples were spliced with output fiber Bragg grating with the excess losses of approximately 3 dB. Using the different fiber length we tried to find an optimal length providing the spectrum with the longest boundary. It is clear that the increase of the length should lead to growth of the loss, but too short fiber cannot provide efficient non-linear conversion.

2.3 Active media
a) Ho-doped fiber amplifier
We have used two samples of Ho-doped fiber with different concentration of the active ions, as a non-linear medium both fibers have the anomalous chromatic dispersion at the pumping wavelength. It means that the supercontinuum should be caused mainly by the cascade Raman scattering in the field of the anomalous dispersion. To use the amplifying properties of the Ho-doped fiber it was pumped by the Yb-doped fiber laser emitting at 1125 nm. Emissions of Er-doped and Yb-doped lasers were combined by wavelength division multiplexer (WDM).

b) Tm-doped fiber amplifier
Output of the laser was spliced with a piece of the Tm-doped fiber. Its emission wavelength of 1.59 µm corresponds to the transmission ³H₆→³F₄ for Tm-ions. Small signal absorption in the corresponding band was as high as 300 dB/m. Waveguide parameters were similar to the characteristics of the telecommunication fiber.

3. Results.
3.1 Ge-doped fiber
We obtained flat output spectrum to 2.7 µm. Average output power was of 0.5 W and the part of power in the range 2-2.7 µm was of 58%. Stimulated Raman scattering is the main effect that leads to broadening of spectrum to the long wavelength range. So fiber with large SRS factor can provide more effective supercontinuum generation in the range 2-2.7 µm. In the heavily germanium doped fiber SRS factor is higher, and losses in this spectral range are less, than in conventional optical fibers. Also in germanium fiber nonlinear factor is higher, that confirms by the short wavelength generation. At the same time these fibers remain to be silica-based ones and can be applied in all-fiber devices as the special nonlinear medium.

3.2 Holmium fiber amplifier.
It was possible to observe the efficient supercontinuum generation in the range of 2.0 – 2.5 µm with the strong depletion of the emission at the shorter wavelength. Very flat spectrum was observed in the range of 2.20 – 2.42 nm where power variation is less than 20%. The maximum average power was measured as 0.35 W. Total output pulse energy is 0.1 mJ with spectral density 10 W/nm.
We have tested the supercontinuum generation in Tm-doped fiber. The corresponding spectrum is shown in fig. 2. One can see that it consists of 3 wide bands. One of them, from 1.55 to 1.7 μm corresponds to the pump emission with non-linear conversion. Second bands centered near 1.8 μm can be attributed to an amplification caused by the $^3F_4 \rightarrow ^3H_6$ transition. Last bands with the maximum at 2.4 μm cannot be explained. Therefore there is reason to believe the existence of the optical transition $^3H_4 \rightarrow ^3H_5$ in the Tm-doped silica based fibers.

**Conclusion.**

All-fiber source of supercontinuum with long-wavelength limit near 2.7 μm was demonstrated. Ho-doped fiber amplifier was used as a non-linear medium of the supercontinuum generator. We have used Tm-doped fiber to enhance the supercontinuum generation under pumping at 1.59 μm. The same source was used for the excitation of Tm-ions. The obtained spectrum occupies the range of 1.85-2.4 μm with the power variation of one decade. The observed spectrum shape allows one to believe the existence of the optical transition $^3H_4 \rightarrow ^3H_5$ in the Tm-doped silica based fibers.

**References.**

Suppression of stimulated Brillouin scattering (SBS) in high power single-frequency linearly-polarized all-fiber amplifiers

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Abstract
High power single-frequency, linearly polarized lasers with nearly diffraction-limit beam quality have been found widespread applications in gravitational wave detection, free space optical communications, range finding, lidar, and coherent beam combining, nonlinear frequency conversion or parametric amplification. Master-oscillator power fiber amplifier (MOPFA) configurations represent one of the most promising paths to efficiently realize the above critical condition at higher power levels for these more demanding applications. The output power of narrow line-width single frequency MOPFA system is limited at hectowatt level because of the onset of stimulated Brillouin Scattering (SBS) effect. In this paper, we report an experimental and numerical study of the SBS-suppression by applying tensile strain and temperature gradients. So far, we present an optimal single-frequency all-fiber amplifier model over 200 Watts with high slope-efficiency of 86% and small M2 factor of 1.3.
We report on the fabrication and investigation of a fiber with a multiply doped core, manufactured with the technique of granulated oxides. The dopants Erbium, Neodymium and Bismuth were selected such that their fluorescence covers a broad spectral range in the infrared (from 1000 nm to 1700 nm) and that they can be simultaneously excited with a single pump laser at 800 nm. The core was co-doped with Aluminum to enhance the homogeneity, since Aluminum increases the solubility of rare earth in glass and thereby prevents clustering of the rare earth ions. In order to further increase the homogeneity and thus to improve the optical quality of the core glass, the core-oxides-mixture powder was three times melted and milled before the drawing process. The investigated fiber exhibited a double-clad structure with a core diameter of 25.5 µm and a cladding of 125 µm. The maximum emitted fluorescence power in the infrared spectral range between 1000-1700 nm of a 9.96 m long fiber piece was ≈660 µW when pumped at 800 nm. By changing the pump wavelength to 976 nm, only Erbium and Bismuth are excited and thus the spectral emission can be manipulated by the pump wavelength.

1. Introduction

Broadband light sources have become indispensable for a multitude of applications, among them spectroscopy [1], microscopy [2], sensing [3] or medical diagnosis. Many of the applications rely on the very short coherence length which is a consequence of the broad spectral distribution and which may be as short as a few microns. Here, we report on the fabrication and investigation of a fiber with a multiply doped core, manufactured with the technique of granulated oxides [4], where we targeted the spectral region from 1000 nm to 1700 nm. In a previous paper [5], we reported on an extremely broadband continuous wave fluorescence light source, which is based on a fiber with a single, multiply doped core pumped by a single pump wavelength. This fiber possessed a spectral gap in the region from 1150 nm to 1300 nm. In addition to Erbium and Neodymium, we used Bismuth as dopant [6] in order to fill this spectral gap. Aluminum was added to enhance the solubility of the rare earths and thus to increase the homogeneity [7]. The envisaged use of the fiber is in the field of broadband amplification. By using a doped fiber as light source, one can use the advantages of fiber based sources, such as the high beam quality, high pump efficiency, compactness, high brightness and high spatial coherence.

2. Fabrication procedure and geometry

The fiber was drawn from a preform that was fabricated based on the technique of granulated oxides [4,5]. The composition of the core-mixture consisted of 98.57 at.% of SiO₂, 1.3 at.% of Al₂O₃, 0.1 at.% of Bi₂O₃, 0.02 at.% Er₂O₃ and 0.01 at.% of Nd₂O₃ [8]. This core-mixture powder was three times melted (with the aid of a CO₂-laser) and milled to increase the homogeneity of the final core glass. This powder was then filled into a pure silica tube with an inner diameter of 17 mm and an outer diameter of 21 mm. This preform was drawn to a fiber-rod with a diameter of approximately 2.4 mm. This fiber rob was then placed and centered in a second 17 by 21 mm silica tube and became the doped fiber core. The remaining space of the second preform was filled with undoped granulated silica (SiO₂). Together with the walls of the first and second silica tube, the undoped granulated silica became the cladding of the fiber. This preform was drawn to a fiber with 125 µm cladding and ≈25.5 µm core. Furthermore, the fiber was coated with a low-index coating to enable waveguiding of the cladding, which results in a so called double-clad fiber structure. The numerical aperture (NA) of the core was <0.1156 and that of the cladding was 0.41. Due to the large core, the core waveguiding was multimode.

3. Experimental and discussion

The fiber was pumped at 800 nm by splicing a fiber-coupled diode to the fiber. Fig.1 shows the spectrum (in the targeted spectral range from 1000 nm to 1700 nm) of a 9.96 m long fiber piece, when pumped with 3.76 W. The four main peaks in this spectrum can be identified. The spectral peak at 1060 nm can be chalked up to the transition \( \text{4}F_{3/2} \rightarrow \text{4}I_{15/2} \) of the Nd³⁺ [9]. Bi³⁺ is responsible for the peak at 1330 nm (the associated transition is \( \text{4}F_{3/2} \rightarrow \text{4}I_{15/2} \) [9]. Er³⁺ produces the peak at 1531 nm, corresponding to the \( \text{4}I_{13/2} \rightarrow \text{4}I_{15/2} \) transition [9]. Bi³⁺ is responsible for the peak around 1100 nm [6]. The spectral output together with the power output was investigated for different pump powers and different fiber lengths, by doing a cutback measurement. In Fig.2 a) the fluorescence output power above 1000 nm (for three different pump powers and four fiber lengths (9.96, 7.0, 4.0 and 0.99 m)) are presented and in Fig.2 b) the
corresponding residual pump power. The maximal output power guided and emitted from the core and cladding was \( \approx 660 \mu \text{W} \) when pumped with 3.76 W, with a corresponding core output (only guided and emitted from the core) of \( \approx 49 \mu \text{W} \). In addition to the excitation with a pump wavelength of 800 nm, we also investigated the spectrum (see Fig. 1) and the output power (see Fig. 2) for an excitation at 976 nm. The fluorescence of Erbium is stronger, since Erbium exhibits a larger absorption cross section at 976 nm compared to 800 nm. There is no fluorescence arising from the Neodymium due to the fact that Neodymium does not absorb at 976 nm. Bismuth also absorbs at 976 nm and shows a broader emission compared to the excitation at 800 nm. For pumping at 976 nm the maximal output power (core and cladding) was measured to be \( \approx 1423 \mu \text{W} \) when pumped with 3.43 W, with a corresponding core output of \( \approx 105 \mu \text{W} \). In addition to the pump wavelength dependence of the fluorescence spectrum, the spectral power density could also be shifted from the infrared to the visible as function of the fiber length or the pump power due to excited state absorption (ESA) and/or energy transfer up-conversion (ETU). Thus and since we have only observed the infrared fraction of the fluorescence, we are not able to make a good conclusion about the measured spectral shape and the corresponding power.

![Figure 1: Infrared fluorescence spectra of a 9.96 cm long fiber piece for an excitation at 800 nm and at 976 nm.](image1)

![Figure 2: a) Infrared fluorescence output power above 1000 nm (guided and emitted from the core and cladding) for four different fiber lengths (9.96, 7.0, 4.0 and 0.99 m) and at two pump wavelengths (800 and 976 nm) for increasing pump power. b) Corresponding residual pump powers.](image2)

References

PROGRESS IN THE FABRICATION OF RARE EARTH DOPED OPTICAL FIBER BY STANDARD AND SOL-GEL DERIVED GRANULATED OXIDES

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We report on improvements in the production of ytterbium (Yb) doped optical fibers by the granulated aluminophosphosilicate oxides method. The doped granulated oxides were prepared by two different procedures: direct mixing of granulated pure oxides and granulate produced by sol-gel. As an alternative to the MCVD technique, the granulated oxides method offers great simplification of manufacturing fibers with flexible fiber geometries and composition. In particular, the sol-gel based method eases the inclusion of P2O5 and thus, in combination with Al2O3, higher dopant concentration of Yb and Er are possible. By sintering the sol-gel material at high temperature eliminated bubbles in the core. The material homogeneity was improved by introducing iterative melting and milling procedures. We fabricated fibers from doped granulated oxides prepared by the two methods and determined the refractive index profile, dopant distribution, crystalline phase as well as background losses.

1. Introduction

Rare earth doped optical fibers are of great significance for many applications including fiber lasers and sensors. Large core Yb2O3 doped optical fibers play an important role in the field of high power fiber lasers [1, 2]. Yb3+ is the preferred lasing ion because of the long lifetime of the excited state, the simple energy-level scheme and the small quantum defect between the pump and laser wavelength. Rare earth doped fibers suffer from high attenuation compared to passive fibers. In order to improve the properties of such fibers, understanding the origin of attenuation is very important. A number of methods have been investigated for integrating rare earth (RE) ions into the silica fiber preforms used for making optical fibers. The most common technique is Modified Chemical Vapour Deposition (MCVD). This common technique has its own geometrical and homogeneity shortcomings [3]. In the recent past, and as an alternative to MCVD technique, we have studied the use of RE doped granulated oxides as active fiber core material. This method offers a high degree of freedom for fiber fabrication (e.g. special fibers geometries, such as leakage channel fibers) and high RE doping concentrations with increased uniformity along the length of the preform, large and homogeneous core sizes, invariable refractive index profile.

2. Methods

In order to manufacture active optical fibers, we followed two approaches to produce doped granulated core material. These are: i) direct mixing of distinct granulated oxides (SiO2, Al2O3, P2O5, Yb2O3) [4]; ii) sol-gel derived doped granulates. To minimize attenuation losses, we produce the granulated material by the sol-gel gel method and add dopants of soluble compounds in organic solvents at low temperature [5]. This yields a higher level of homogeneity down to the molecular level and hence lowers scattering losses. Furthermore we increase the homogeneity by milling and re-melting the part of the material that will constitute the active core material. Because of its high porosity sol-gel material easily adsorbs water and impurities; the optical quality of the material can be improved by appropriate thermal treatment at temperatures up to 1500°C. In addition, heating consolidates the material which results in a reduction of the porosity and in the elimination of bubbles in the fiber. After iterative melting and milling, doped granulated core material was obtained.

The optical properties of the fabricated fiber was characterized by different analytical techniques: energy dispersive x-ray (EDX), electron probe microanalyses (EPMA), x-ray diffraction analysis (XRD) and refractive index profilometry, (RIP).

3. Results

The fabricated active granulated oxides with active core matrix composition of 94.7 mol% SiO2, 3mol.% Al2O3, 2 mol% P2O5 and 0.3 mol% Yb2O3 were added into a preform silica tube with sealed bottom end. The XRD pattern of the doped granulated core material showed that there was no crystalline peak observed. It was drawn to a 63/250 μm core/cladding ratio with a measured refractive index of Δn = 5*10^-3 having a fluctuation of 4*10^-4 as shown in Fig. 1. This fiber was piecewise homogeneous with sporadic strong scattering centres. The measured average attenuation losses between the strong scattering centres, determined by the cutback method at 633 nm, was 0.35 dB/m. Further efforts will be needed to reduce the background losses in order to increase lasing properties. Therefore, our present focus is on minimizing the strong scattering centres.
4. Conclusion

Active granulated optical core materials were produced by the sol-gel method. Modification of the active core materials were performed by repeated milling and melting using CO2-laser and their optical quality was improved. The elimination of bubbles due to the sintering process was a further achievement. Our measurements using refractive index profilometry reveals a flat index profile with low transversal fluctuations and without central dip. Piecewise, the fiber was homogenous with little scattering centers. The average scattering losses measured on pieces between consecutive strong scattering centers was 0.35dB/m. Work on the origin of the residual strong scattering centers in order to further improve the fiber quality is in progress.

References

Silicon nanoparticles (SiNPs) obtained by mechanical grinding of microporous silicon have been used for visualization of living cancer cells in vitro. It was found that SiNPs could penetrate into the cells without any cytotoxic effect. The cell cytoplasm was observed to be almost filled by SiNPs, which exhibited bright photoluminescence at about 750 nm. SiNPs suspended in water could also act as photosensitizers of singlet oxygen generation, which could be used in the photodynamic therapy of cancer, and sonosensitizers for the ultrasound therapy. These properties are discussed in view of possible applications of SiNPs in theranostics (therapy and diagnostics).

1. Instructions
It is known that silicon (Si) plays a dominant role in electronics industry, but it also can be rather important in biomedicine [1-3]. Very low levels of the genotoxicity and teratogenic risks of SiNPs were demonstrated in vivo [4]. SiNPs were shown to act as a photosensitizer of the singlet oxygen (SO) generation [5], which can be used for the photodynamic therapy (PDT) of cancer [6]. Also recently it has been found, that combined action of SiNP and ultrasound irradiation could lead to the destruction of cancer cells in-vitro [7]. In the present paper SiNPs prepared by mechanical grinding of microporous silicon were examined for bioimaging of cancer cells. Also, similar SiNPs were used as photosensitizer of the SO generation and sonosensitizer of ultrasound effect to destroy cancer cells in-vitro.

2. Experimental Details
SiNPs were fabricated by high-energy milling of microporous silicon (PSi) films in water by using a planetary-type mill FRITSCH «Pulverisette 7 premium line». The PSI films were formed by the standard method of electrochemical etching of bulk silicon (c-Si) 10 Ω·cm in a solution of HF (48%):C2H5OH at the current density of 60 mA/cm² and etching time of 60 min. The PSI films were separated from c-Si substrates by applying a short pulse of the current density of 600 mA/cm². The size of SiNP was determined by using a transmission electron microscope (TEM) LEO912 AB OMEGA, as well as by the method of dynamic light scattering (DLS) using a Malvern Zetasizer Nano ZS device. Typical DLS spectra shown in Figure 1 demonstrate that the dominant size of SiNPs prepared from PSi is about 75 nm that ensures their penetration into living cells.

![Figure 1: Size distribution of SiNPs for the samples prepared from PSi and c-Si measured by DLS.](image)

The composition of surface coating of SiNP was studied with an infrared (IR) spectrometer Bruker IFS 66v/S. Before measuring the IR spectra, the PSI films and SiNPs were dried in air and evacuated at 10⁻³ Torr. The IR spectra of suspensions were recorded using an ATR unit. According to the IR spectra the grinding of PSI in water resulted in the hydrogen losses and partial oxidation of SiNP surfaces. The oxide coverage of SiNP causes obviously the hydrophilic properties of its surface. PL was excited by a nitrogen-laser radiation (wavelength 337 nm).

_in-vitro_ experiments were carried out with cancer cells Hep-2 (human lung cancer), CHO (Chinese Hamster Ovary) and 3T3 NIH (modified mouse fibroblasts). The fluorescent imaging study was carried out with aqueous suspensions of SiNPs introduced to the cancer cells. After the incubation period and before the observation, the cells were rinsed by...
water to remove SiNPs. The incorporation of SiNPs inside the living cells was monitored over several hours. Under UV light excitation the cells marked by SiNPs were rather bright in order to be distinguished from the autofluorescence background.

3. Results and Discussion

Typical PL spectrum of the aqueous suspension of SiNPs is shown in Figure 2. The PL quantum yield for initial PSi layer was above 5%. The PL of suspension of SiNPs at concentration about 10 mg/l PL could be easily observed with a naked eye (see inset in Figure 2).

In-vitro experiments showed that SO photosensitized by SiNPs suppressed the proliferation of cancer. The DNA analysis of the cancer cells after the interaction with photoexcited SiNPs provides evidences of the apoptosis mechanism of their death. These results demonstrate that SiNPs can be considered as photosensitizer in photodynamic therapy (PDT) of cancer and other tumors. It was revealed that the aqueous suspensions of SiNPs with concentration up to 2 g/l were non-toxic for mouse fibroblasts and human cells in darkness.

SiNP was found to exhibit properties of sonosensitizer, i.e. a substance for an activation of the ultrasound-induced heating of water and biological systems. A destruction of the cancer cells under ultrasound irradiation in the presence of SiNPs at the concentration below 1 g/l has been observed in-vitro. This effect can be explained as follows: (1) the cancer cells die because of their local heating induced by oscillating motion of nanoparticles, i.e. because of local hyperthermia; (2) nanoparticles act as “nano-scalpels,” which can destroy mechanically the cells; (3) nanoparticles can play a role of cavitation centers, which initiate thermal and mechanical damages in cancer cell.

Figure 2: Typical PL spectrum of SiNPs prepared from microporous PSi in aqueous suspension. Inset shows the image of a vessel with the suspension of SiNPs under excitation with UV laser.

4. Conclusions

The obtained results demonstrate that nanoparticles prepared from microporous silicon are promising for biomedical applications as diagnostics and therapy. The can be used in both bioimaging and photodynamic therapy of cancer. Also the sonosensitizing properties of silicon nanoparticles are promising for the therapy of tumours.

5. Acknowledgements

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References

We present Raman studies of several kinds of polymeric blends, such as mechanical and reactor blends of polyethylene (PE) and isotactic polypropylene (PP), and reactor blends of PE with random ethylene/1-hexene copolymer (CEH). We show that Raman spectroscopy is a powerful tool for the quantitative analysis of supramolecular structure of these materials in terms of the blend composition, phase and conformational order of macromolecules.

It is known that the mixing of two polymers makes it possible to create materials with new set of characteristics and allows the target control of their structure and properties in a wide range. Such a modification of polymer materials is promising and economically effective, since it does not require new production facilities. Both components in a polymer blend can form different phases and affect the crystallization process of another component as well as the formation of overall supramolecular structure. Currently, creation of polymer blends is important branch of polymeric industry. The properties of any polymeric material depend strongly on a number of structural characteristics, for example, the phase and conformational compositions, size of the crystallites, the chemical composition. Therefore, it is desirable to have techniques, which allow the determination of maximum structural characteristics. The Raman spectroscopy is a convenient and highly effective method for the structural analysis of conformational and phase orders in neat PE. However, the Raman spectroscopy is very seldom used to study PE-based blends. In our contribution, we present Raman studies of a number of PE-based blends, such as mechanical and reactor blends of PE and isotactic PP, reactor blends of PE with CEH. We demonstrate that Raman spectroscopy allows non-destructive way to determine many characteristics of supramolecular structure in these blends (the relative content of PP/PE, an amount of crystallites PE and PP, the proportion of trans-gauche- conformers in PE component of the blends).

For instance, Fig. 1 shows Raman spectra of the PE/PP blends, produced by mechanical mixing in melt at 200°C. The figure also presents the spectra of neat PE (the melting temperature is 118°C) and neat isotactic PP (the melting temperature is 176°C). The line at 1295 cm⁻¹ corresponds to the vibrations of PE molecules in trans-conformation in both crystalline and amorphous phases. High-frequency shoulder of this line at about 1305 cm⁻¹ relates to the vibrations of PE molecules in gauche-conformation in the amorphous phase. The line at 1330 cm⁻¹ corresponds to the vibrations of PP isotactic molecules in both the crystalline and amorphous phases. We showed that the integral intensity ratio \((\frac{I_{1295}+I_{1305}}{I_{1330}})\) is proportional to the ratio of the mass contents of PE and PP in the blends. Thus, this intensity ratio can be used to analyze the PE/PP blend composition.

The lines at 809 and 1415 cm⁻¹ relate to the vibrations of molecules in the crystalline phases of isotactic PP and PE correspondingly. Integral intensity of each of these lines determines the degree of crystallinity of corresponding polymer, relative to the internal reference intensity in the spectrum of each polymer. The line at 841 cm⁻¹ corresponds to the vibrations of isotactic PP molecules with conformational defects. Based on the analysis of the lines at 809, 841, 1295, and 1415 cm⁻¹, we concluded that the crystallinity and conformational composition of PP and PE molecules strongly depend on the relative content of the blend components and the melting temperature.

Fig. 2 presents Raman spectra of neat PE, neat CEH with 37 mole % of 1-hexene, and two PE/CEH reactor blends. The lines at 1062 and 1130 cm⁻¹ are assigned to the vibrations of trans-conformers, localized in both the crystalline and amorphous phases of PE. The broad band at about 1080 cm⁻¹ corresponds to the vibrations of gauche-conformers in the amorphous phase of PE. Based on the analysis of intensities of the lines at 1060, 1080, 1130, 1295, and 1415 cm⁻¹, we can conclude that increase in the CEH content leads to the decrease in the content of the PE-like orthorhombic crystalline phase and in the content of trans-conformers in the amorphous phase. Simultaneously, the increase in the content of gauche-conformers in the amorphous phase is observed.

Analysis of Raman spectra of a number of series of the PE/CEH reactor blends leads us to the general conclusion that the phase and conformational order of macromolecules decreases with the increase in the CEH content in the blend as well as with the increase in 1-hexene content in the CEH.

In summary, we concluded that Raman spectroscopy is a powerful tool to characterize the structure of polymer blends in terms of chemical composition, phase and conformational order of macromolecules.

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Fig. 1. Raman spectra of neat PE, neat isotactic PP, and the PE/PP blends

Fig. 2. Raman spectra of neat PE, neat CEH with 37.0 mole % of 1-hexene, and the PE/CEH blends
FLUORESCENT PROPERTIES OF THE KINDLING FLUORESCENT PROTEIN (KFP) AT ACIDIC PH VALUES

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Kindling fluorescent protein (KFP) is the photoswitchable protein which can be used in high-resolution microscopy and as a quencher in FRET-sensors. Fluorescent properties of KFP depend on pH value. In this paper we investigate the influence of pH on the spectral properties and kindling/quenching ability of KFP in the acidic pH region.

Shift in the acidic region leads to the increase of fluorescence intensity of KFP over time. The excitation spectrum has a new peak near 455nm, giving two peaks - 530 and 590nm – in emission spectrum. We can assume that this maximum corresponds to the appearance of protonated form of the KFP chromophore.

At acidic pH irradiation of KFP with green light doesn’t lead to fluorescence increase, while blue light doesn’t quench the fluorescence. It means that KFP is also in the bright form, and there is no conformational states of protein which can be quenched by blue light.

Analysis of fluorescence decay curves of KFP in H2O and D2O showed the presence of the kinetic isotope effect, which can be caused by the proton transfer from solvent molecules to the KFP chromophore, confirming the hypothesis that in the acidic pH region protonated form of KFP chromophore appears.

Introduction

Fluorescent proteins are widely used as genetically encoded fluorescent markers for gene expression and localization of proteins in cells, as well as biosensors. Discovery of the photoswitchable proteins that change their properties upon irradiation with light of a certain wavelength, allowed to develop innovative methods of high-resolution microscopy. At low light intensities photoswitchable proteins with a low quantum yield before the photoactivation can be used as quenchers in FRET-sensors. Photoswitchable protein asCP595 was isolated from the anemone Anemonia Sulcata. This protein is weakly fluorescent (φ <0,001) chromoprotein with a maximum fluorescence at 595 nm. However, upon intense irradiation with green light this protein switches to the fluorescent form, significantly increasing the fluorescence quantum yield. Photoactivation of natural asCP595 is reversible, since switching off the green light irradiation leads to a gradual, and blue light irradiation – a rapid transition to nonfluorescent form of the asCP595. Inclusion of Ala148Gly mutation in asCP595 leads to protein named KFP, which has better contrast and increased relaxation time.

One of the factors that influence the spectral characteristics of fluorescent proteins is the pH value. Changing the pH shifts the equilibrium between the anionic and neutral forms of the chromophore. This phenomenon can be explained as the change of the protonation state of aminoacids near the chromophore affects the fluorescent properties of the protein[1].

Rusanov et al. [2] shown that the shift of pH to the alkaline region leads to a substantial change in the spectral characteristics of KFP. Thus, at neutral pH KFP practically does not fluoresce, whereas at pH above 9 a significant increase in fluorescence intensity can be observed, and this phenomenon is completely reversible. The absorption maximum at higher pH is shifted to shorter wavelengths, while the absorption decreases. These phenomena are interpreted by the authors as a shift of equilibrium between the different fluorescent and nonfluorescent conformations of the protein.

In this paper we investigate the influence of pH on the spectral properties of KFP in the acidic pH region. As in the case of alkaline pH, there is the appearance of new conformations of the protein, causing a change of its fluorescent properties.

Materials and Methods

The purified protein KFP was dialysed against the 0.1 M CH3COONa, 0.2 M CH3COONH4, pH 5,7 buffer. Then the protein solution was titrated to the desired value of pH (from 5.3 to 3.3) and measurements of the absorption spectra (Cary 300, “Varian”, USA), fluorescence excitation at λem = 640 nm and emission spectra at λexc =455 and 530 nm (Cary Eclipse, “Varian”, USA).

Photoswitching and quenching of KFP was carried out by irradiating a sample of the protein in the 20 mM Tris-HCl, 150 mM NaCl, 500 mM Imidazole, pH 4.02 buffer with green (532 nm, power 5 mW) and blue (405 nm, power 80 mW) lasers. Fluorescence was measured by using the ”Spektr-Cluster” setup (www.cluster.orc.ru). The source of the excitation light in this setup is a laser with a wavelength of 532 nm, coupled to optical fiber diameter of 110 µm, and detection is performed by fiber-optic catheter, composed of six light-harvesting fibers with 110 µm diameter, located around the source of the excitation light.

KFP quenching kinetics were obtained by simultaneously focusing the green and blue lasers on a KFP sample in the quartz Hellma cell with 0,3 mm optical path. The spectra were measured every 700 ms, and the exposure time was...
50 ms. Beams crossing were adjusted by obtaining the minimum fluorescence intensity of the KFP sample during irradiation with both lasers. Laser beam power was measured using a power meter 2936-C (Newport).

To determine the kinetic isotope effect sample of KFP in the buffer 20 mM Tris-HCl, 150 mM NaCl, 500 mM Imidazole, pH 7.6 was titrated to pH 3.94, and then 10 µl of the sample was added to 90 µl of H2O and D2O, respectively. Lifetimes were measured by TCSPC method on FluoTime 200 (PicoQuant GmbH, Germany) using a picosecond laser (wavelength 405 nm) as a source of excitation light. Data analysis was performed using FluoFit software (PicoQuant GmbH, Germany). Kinetics of decay were captured at 520 nm wavelength.

Results and discussion

pH-dependence of fluorescent properties of KFP

At neutral pH KFP practically does not fluoresce, which is consistent with previous results [2]. Shift in the acidic region leads to the increase of fluorescence intensity of KFP over time. Excitation peak around 450 nm in case of pH greater than 4.7 is not individual, whereas at pH 4.5 and below excitation spectrum has two separate peaks - 450 and 570 nm.

Also at pH lower than 4.5 the fluorescence intensity of KFP increases more than 2 times at 530 nm excitation, while excitation at 455 nm results in more than an order of magnitude increase of intensity. As for the absorption of the KFP sample, the intensity of the peak at 560 nm decreases with time, whereas the absorption at 450 nm increases, which corresponds to a gradual increase in the fraction of protein which fluoresce when excited at this wavelength.

In addition, there is a shift of the fluorescence maximum to longer wavelengths over time.

At low pH, the fluorescence of the protein decreases over time, indicating that KFP was denatured. While shifting the pH from acidic to neutral region the rate of increase of fluorescence KFP also increases, reaching a maximum at pH 4.3, and at pH 7.3 the intensity is almost zero, which corresponds to the transition to nonfluorescent form of KFP.

The absorption spectra of the KFP show a decrease in the intensity of the absorption peak at 570 nm over time, whereas intensity of 455 nm peak gradually increased.

Thus, in acidic pH region there is a spontaneous kindling of KFP. The excitation spectrum has a new peak near 455 nm, giving two peaks - 530 and 590 nm – in emission spectrum. The highest intensity of KFP’s fluorescence increase KFP is observed at pH 3.9 and 4.3 for the 530 and 590 nm peaks, respectively. According to the changes in absorption spectrum of KFP, where 570 nm peak decreases over time, and 455 nm peak increases, it can be suggested that the at acidic pH small fraction of the protein undergoes structural changes that lead to the appearance of intense fluorescence upon excitation at 455 nm. In the fluorescence spectra of KFP, obtained by excitation at 455 nm, in addition to the characteristic maximum around 600 nm, there is another, not previously described - about 530 nm. We can assume that this maximum corresponds to the appearance of protonated form of the KFP chromophore.

Kindling and quenching of KFP in acidic pH region

According to Rusanov et al. [2], at pH 8.8 KFP practically does not fluoresce, whereas under intense green light intensity of its fluorescence increases several times. While shifting to the alkaline region the appearance of bright fluorescent components, which are not kindled by the intense green light, can be observed. At acidic pH values there is a similar pattern - KFP initially has a high fluorescence quantum yield, and the irradiation by green light increases fluorescence by no more than 10%. Irradiation by green laser followed by switching on the blue laser (405 nm wavelength) does not lead to fluorescence quenching of KFP. The same result was obtained while irradiating the sample with green and blue lasers simultaneously. If we irradiate KFP only by blue laser, the fluorescence intensity increases, but to a lesser extent than in the case of a green laser. This phenomenon does not depend on the power of blue laser. Thus, at acidic pH KFP is in the bright form, and its irradiation with blue laser doesn’t lead to fluorescence quenching, in contrast to the alkaline pH region. So, at acidic pH there is no form of KFP which can be quenched by blue light.

Fluorescence decay kinetics of KFP in H2O and D2O

Analysis of fluorescence decay curves of KFP in H2O and D2O showed that the initial curves for these samples are different, namely, the fluorescence decay kinetics of the sample in D2O is somewhat delayed compared with the kinetics of the sample in H2O. These results indicate the presence of the kinetic isotope effect, which confirms the hypothesis that in the acidic pH region protonated form of KFP chromophore appears. That proton transfer from solvent molecules to the KFP chromophore causes the difference in the fluorescence decay kinetics of KFP in H2O and D2O.

References


OPTICAL PROPERTIES OF SILICON NANOWIRE ARRAYS FORMED BY METAL-ASSISTED CHEMICAL ETCHING

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Arrays of silicon nanowires (SiNWs) with mean diameters of about 50–200 nm were formed on crystalline silicon (c-Si) substrates by using metal (Ag)-assisted chemical etching in hydrofluoric acid solution. The infrared absorption, photoluminescence, Raman scattering of the formed samples were investigated to reveal dependences on the preparation conditions. The formed SiNW layers under laser excitation at 1.06 µm exhibit efficient band-gap-related photoluminescence (PL) at 1.1 µm as well as enhanced Raman scattering on the optical phonons at 520 cm⁻¹. Under laser excitation with UV light it is observed the PL band at 700 nm, which is related to the radiative recombination of excitons confined in small Si nanocrystals on SiNWs surfaces.

1. Instructions

Recently it was reported a growth of quasi-ordered SiNWs with diameters from 10 to 200 nm, by using a metal-assisted chemical etching (MACE) of c-Si wafers in HF-based solutions [1]. The MACE possesses some advantages in comparison with other methods of the SiNWs formation because of possibilities to grow SiNWs on both bulk c-Si wafers and thin Si layers (e.g. multi-, nanocrystalline or amorphous) on glass substrates12. It was found that SiNWs formed by the MACE method showed room temperature photoluminescence (PL) in the visible [1,2] and near-infrared [3] spectral ranges. In the present work, the structure, PL and Raman scattering of SiNWs prepared by MACE method were investigated paying special attention to the influence of growth conditions on the efficiency of the PL and Raman scattering signals.

2. Experimental Details

SiNWs were grown by the MACE method in several stages as (i) deposition of metallic silver (Ag) layers or nanoparticles on c-Si substrate, (ii) red-ox reactions at Ag/Si interface, and (iii) chemical removal of residual Ag spices. Well-ordered SiNWs were formed by using substrates of lightly doped (1–20 Ω·cm) (100)-oriented c-Si wafers. The structure of the formed samples was studied by using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The optical properties of the samples were investigated at room temperature in air. SiNW diameters are ranged from 50 to 200 nm (see Fig.1). It was possible to change the SiNW thickness and orientation by using c-Si substrates with different doping level and surface orientation, respectively. The SiNW length is controlled by the etching time and it could be varied from 1 to 200 µm under our experimental conditions. Typically, the length of about 20 µm was achieved for the etching time of 40 min.

Figure 1: Typical cross-sectional SEM image of PSi layer formed on (100) p-Si wafer.
3. Results and Discussion

A broad near-infrared PL band at 1120 – 1150 nm and a sharp Raman scattering line at 520 cm\(^{-1}\) were observed for PSi samples under excitation at 1.06 \(\mu\)m. Both the PL and Raman scattering were found to be significantly stronger than those of c-Si substrate (see Fig.2). If one takes into account the difference in the thickness of PSi layer (typically 10-50 \(\mu\)m) and c-Si substrate (about 400 \(\mu\)m) the relative enhancement of the PL and Raman scattering intensities for PSi in comparison with c-Si can exceed 50 times. The observed effect can be explained by strong enhancement of the excitation efficiency in PSi because of an effect of the partial light localization in SiNW ensembles [3].

In contrast to the PL properties, the Raman peak intensity depends on the laser power practically linearly both for heavily and lowly doped single crystalline initial wafers and for all samples of SiNWs. The obtained results can be understood by taking into account the structure of the prepared PSi. The thickness of SiNW layer (SiNW length) was about tens \(\mu\)m. The absorption coefficient of c-Si at wavelength of 1 \(\mu\)m nm does not exceed 100 cm\(^{-1}\), thus, the light absorption does not prevent whole SiNW array from taking part in the PL and Raman signal generation. The fact that the PL intensity of PSi increase by different factor than the corresponding Raman signal indicates a role of the carrier recombination for the PL properties.

The formed SiNW arrays demonstrate a strong decrease of the total reflectance below 1% in the spectral region of 300÷1000 nm and the samples look like “Black Silicon”, which can be used as antireflection coating in photovoltaic applications. The prepared SiNWs exhibit efficient PL in the spectral region of 600-1000 nm, which is related to the radiative recombination of excitons confined in small Si nanocrystals on SiNW surfaces. It is also shown the biocompatibility of SiNWs and possibilities of their applications in bioimaging of living cells.

4. Conclusions

SiNW arrays composed by quasi-ordered SiNWs with mean diameters from 50 to 200 nm and length varied from 0.1 to 200 \(\mu\)m were grown by metal-assisted chemical etching. The structure, PL and Raman scattering properties of SiNWs are strongly dependent on the doping level and surface orientation of the c-Si substrates. It was observed multiply enhancement of the intensities of PL and Raman scattering of SiNWs in comparison with the corresponding c-Si substrates under excitation at 1.06 \(\mu\)m. The observed effects can be explained by the partial light trapping in SiNW arrays and demonstrated new possibilities for random lasing medium with low generation thresholds, molecular sensors on toxic gases and other devises for nanoelectronics and optoelectronics.

5. Acknowledgements

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References

GENERATION OF NANOSECOND PULSES AT 6.45 µm BY DIFFERENCE FREQUENCY MIXING IN AgGaS2 AND ZnGeP2 FOR SOFT TISSUE ABLATION

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Abstract:

The Mid-IR wavelengths of 6.1 and 6.45 µm, coincide with the absorption bands of Amide-I and Amide-II in proteins. Efficient laser ablation of biological tissues, with minimum collateral damage, has been observed at these wavelengths, using Free Electron Lasers. Much work is now devoted to the development of table-top laser operating at these wavelengths for medical applications.

In this work, we describe the performance of a Nd:YAG laser pumped KTP optical parametric oscillator (OPO). The signal and idler output of the KTP-OPO are mixed in AgGaS2 and ZnGeP2 to generate nanosecond pulses emitting at 6.45 µm by difference frequency generation. We compare the performances of this nanosecond laser source with previous described synchronously pumped CSP picosecond OPO for the ablation of soft tissue and demonstrate that these table top solid state lasers can be viable alternatives to free electron lasers for medical applications in the Mid-IR.

1. Introduction

Investigations on tissue ablation are usually carried out using infrared (IR) laser sources such as Ho:YAG (2.1 µm), Er:YAG (2.94 µm), and CO2 (10.6 µm) [1-3]. For these wavelengths, water is the dominant IR absorber. IR spectrum of proteins is dominated by peptide bonds (O=C-N-H) absorption. The most active of its vibrational modes are the C-O stretch at 6.1 µm, referred to as the Amide-I, and the C-N deformation at 6.45 µm, referred to as the Amide-II. Laser irradiation at the wavelengths between 6.1 and 6.45 µm, entails the denaturation of the protein structure and the explosive vaporization of water. Because the IR absorption of proteins far exceeds that of water [4] at these wavelengths, efficient tissue ablation, with low collateral damage, is observed when using free electron lasers (FELs) tuned to ~6 µm as IR source [5]. However, FELs require dedicated facilities, considerable expertise for their operation, and high costs, which severely limit their clinical applications. Novel IR laser sources covering the wavelengths of interest, like optical parametric oscillators (OPOs), DFG systems are currently developed as alternative to FELs. Thus, we aim at developing a simple, robust, high power, and stable IR laser sources frequency tunable around ~6.5 µm. In addition to the effect of the wavelength, other parameters, such as the macro- and micro-pulse durations, the pulse repetition rate, and its fluency, also play significant roles in soft tissue ablation efficiency. For example, thermal confinement will occur when the pulse duration is shorter than the heat diffusion time to the volume surrounding the irradiated area. In our previous work, we described the performance of a 6.45 µm synchronously pumped optical parametric oscillator (OPO) using type I and type II phase matching in a silver thiogallate (AgGaS2 or AGS) and non-critical phase matching cadmium silicon phosphade (CdSiP2 or CSP) crystals quasi-collinearly pumped at 1064nm by a 25Hz picosecond passive and active mode-locked Nd:YAG laser[6,7].

In this paper, we discuss the performance of AGS-based, and ZGP-based DFG stage with an idler wavelength of 6.45 µm which are pumped by a nanosecond Nd:YAG pumped Potassium Titanyl Phosphate (KTP)- based OPO. These performances are compared to those of previous CSP-based OPO emitting at 6.45 µm.

2. Experimental setup:

The scheme of the laser setup is described in Fig.1. It consists of a 10 Hz flash lamp-pumped Q-switch Nd:YAG laser emitting at 1.064 µm. It is followed by a KTP based OPO enabling to generate an idler and signal beams continuously tunable between 1.5 and 3 µm. These two output waves are mixed in type II AgGaS2 (10x8x20 mm) cut at θ=42°, and
type I ZnGeP2 (8x10x20 mm) cut at θ=56° and ϕ=0°, to generate mid-IR tunable radiation from 5 to 12 µm by difference frequency generation process.

Figure 1: Schematic diagram of the DFG system.

We compare the performances of the DFG stage fitted with either AgGaS2 (AGS) or ZnGeP2 (ZGP) by measuring the damage threshold and slope conversion efficiency as a function of the pump average power. These experimental tuning ranges are compared to the theoretical tuning ranges calculated using the Sellmeier equations (see Fig.2). We compare the performances of this nanosecond laser to those of the CSP picoseconds laser described previously [6, 7] for soft tissue ablation and demonstrate that these top table laser can be alternative to free electrons laser for surgical applications at 6.45 µm.

Figure 2: Theoretical tuning curves of AgGaS2 (type II) and ZnGeP2 (type I)

References

Periodically poled lithium niobate crystals can be utilized in nonlinear-optical spectral brightness detectors of terahertz range. In this paper characteristics of detectors were determined by analyzing spectra of spontaneous parametric down- and up-conversion in these crystals.

1. Introduction

Terahertz range attracts considerable attention today due to its possible applications. The further improvement of generation and detection schemes is needed in order to meet the requirements of technology.

There is a promising method for measuring the absolute value of the brightness of terahertz (THz) waves by utilizing quantum fluctuations of electromagnetic field. This method is based on the one proposed by D.N. Klyshko for the infrared range. The method involves the parametric frequency conversion in a nonlinear medium, which allows one to transform THz radiation (at the frequency $\omega_{THz}$) into the optical (“signal”, at the frequency $\omega_s$) wave. The pump beam at the optical frequency $\omega_p = \omega_s + \omega_{THz}$ is required for the method to function. By measuring the spectrum of the signal wave, one can calculate the brightness of the THz wave. The advantages of this approach are the following. First, no calibrated sources of terahertz radiation are needed to determine the absolute value of the brightness. Second, the experimental setup needn’t be cooled to the nitrogen or helium temperatures. All the mentioned above makes this method to be of interest to terahertz science and technology.

2. Crystals for terahertz detectors

The detectors described above utilize nonlinear-optical crystals with a periodical or specially designed aperiodical domain structure that provides the frequencies of signal and idler waves to fall into the range required. The usage of the periodically poled crystals allows one to increase the length of the crystal that generates the signal wave radiation constructively.

It can be shown that the signal wave brightness $B_\omega = \frac{h\omega_3^3}{8\pi^2c^2}N_k$ (in a parametric frequency conversion process between pump and idler waves) has the following dependency from the detector crystal parameters ($N$ is the number of photons per mode of radiation):

$$N_k = \frac{4\pi^2E_0^2}{c^2n^3n_{THz}} \cdot \frac{\omega_3\omega_{THz}}{\alpha_{THz}} \cdot L^2 \cdot e^{-\alpha L/2} \cdot \left[T(\Omega)\right]^2 \cdot N_{THz},$$

where $n$ stands for the refractive index, $\alpha$ - for the absorption coefficient, $L$ - for the crystal length, $E_0$ - for the pump wave amplitude; $T(\Omega)$ is a nonlinear transfer function (T-function), which is dependent from the domain structure of the crystal. It is also shown, that all the influence of the spatial modulation of the second order nonlinear susceptibility $\chi^{(2)}$ can be described by the only functional parameter - T-function. It makes this function the universal characteristics of the aperiodically poled crystal. Nonlinear transfer function can be measured directly via studying the spontaneous parametric down conversion spectra corresponding the THz frequency range of the idler waves.

Thus one can determine the spectral characteristics of the detector by simply measuring its T-function. This paper discusses the experimental procedure of periodically poled lithium niobate (PPLN) characterization, which implies measuring the T-function and comparing real crystals with various domain structure quality and different periods. The example of corresponding spontaneous parametric down-conversion (SPDC) spectra is given. The following typical areas are presented in Fig.1: the horizontal line in the center of the picture corresponds to the scattered pump wave; the Stokes scattering signals are located below it, the Anti-Stokes wave signals are observed above. On the left, the signal wavelength is presented, at the bottom, the scattering angle is. Two horizontal lines at the upper and lower parts of the spectrum correspond to scattering by the A-phonon resonance in PPLN at approximately $232 \text{ cm}^{-1}$. 

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Figure 1: The typical example of the SPDC spectrum in periodically poled lithium niobate.

References
NANOSTRUCTURED ALUMINA OXYHYDROXIDE AND COMPOSITES: DIELECTRIC PROPERTIES IN THZ RANGE

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Development of practical applications of sources, detectors, convertors and other devices in terahertz (THz) range requires continues improvement of their functional properties and search for new materials. Nanostructured objects allowing introduce new properties to the bulk materials tailoring them for certain practical applications. As an example, several works showed perspectives of practical use of porous silicon in THz range [1-4]. In this work the optical properties of a novel material – nanostructured alumina oxyhydroxide (NOA) and some related nanocomposites were studied in THz range.

NOA materials possess high specific surface ~300 m²/g with the structure consisting of alumina nanofibrils integrated into the 3D network [5]. The refractive index n and absorption coefficient α of the NOA samples in THz range were measured by a standard time-domain technique [6] and evaluated using the Bruggeman effective medium approximation [7] (see Fig.1). Influence of the physically absorbed water on the fibrils’ surface on the n and α spectra was studied. THz spectra are shown to be sensitive to structural modifications of the samples – both phase transitions and presence of water on the fibrils’ surface.

Figure 1: Refractive index n (a) and absorption coefficient α (b) of the NOA sample in THz range

References
APPLICATION OF PHOTOTHERMAL AND PHOTOACOUSTIC SPECTROSCOPY FOR THE MONITORING OF AQUEOUS DISPERSIONS OF CARBON NANOMATERIALS

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Photothermal and photoacoustic spectroscopy will be used for the chemical analysis, estimation of physicochemical properties of aqueous dispersions of fullerenes and nanodiamonds as promising biomedical nanosystems.

Unique properties of carbon nanomaterials (such as fullerenes and nanodiamonds) find various applications in several branches of science and technology. They are used in the creation of composites and catalysts. Especially important are biological and medical applications. These substances are used as contrast agents, antibiotics, they are promising against AIDS and cancer and in cellular surgery, as antioxidants and enterosorbents [1]. As well, fullerene clusters of certain size may create an antiviral cell barrier [1]. The area of medicine applications of nanodiamonds is even broader than that of fullerenes [2].

Aqueous solutions of nanocarbon dispersions are the most needed in medicine. Both nanodiamonds and fullerenes form colloidal solutions. It is strongly necessary for biomedical purposes to know concentration of nanodiamonds and fullerenes in solutions and colloidal particle sizes. The methods used for the last aim, dynamic light scattering and low-angle neutron scattering, have some significant drawbacks like very complicated data-handling routines and the problem of scattering on large particles and do not show satisfactory results in all cases. We use novel methods of absorption spectroscopy as methods for estimating size and concentrational dependences in dispersions exemplified by nanodiamonds and fullerenes.

Recently, the progress in laser technologies has provided a sound basis for compact optical schemes and commercial applications of photoacoustic (PAS) and photothermal (PTS) spectroscopies in analytical and physical chemistry. However, in spite of a vigorous discussion of the advantages of these methods and successes in the field of analytical chemistry, their use for investigation side-by-side are very limited, although the methods, having many similarities, are rather complementary rather than competing. In this study, we use PAS/PTS measurements for fullerene and nanodiamond suspensions at high and trace level of constituents in various media (aqueous solutions and organic solvents). These disperse media are characterized by a multitude of conversion mechanisms, with the main feature of their simultaneous and competing character. Moreover, the existing of particles with constantly changing configuration provides a random constituent of the signal. These features were observed as functions of dynamic (response profile) and statistic (amplitude fluctuation) parameters of PAS/PTS signals and disperse-phase parameters. The possibilities of spatial scanning and multi-wavelength PAS/PTS toward this aim will be discussed. Also we studied high-energy laser radiation influence on nanodiamond and fullerene disperse systems.

Another aim of the study is to develop the methodology for the preparation and characterization of aqueous fullerene dispersions with pre-determined cluster size and physicochemical properties. We will use a combination of novel preparation techniques used in analytical chemistry and PAS/PTS for monitoring, backed up by other state-of-the-art spectrochemical methods like UV/Vis/NIR/MIR spectroscopy and chromato-mass-spectrometry for chemical properties and cluster size of fullerenes in aqueous solutions. This prediction can be used to improve lead identification and optimization for fullerene-based medicines.

To date, we have worked out a technique for making aqueous fullerene dispersions and quantified the residual organic solvent to approve the biosafety of suspensions. Under development is the assay for preparing aqueous dispersions with certain fullerene cluster sizes without organic solvents. The results on particle sizes and their monitoring and regulation of fullerene clustering by PAS/PTS will be obtained. We expect even a wider use of our findings as many these patterns are valid also for other nanoscale systems such as nanodiamonds. Specific results will be presented and discussed.

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References

BOUNDARY CONDITION EFFECT ON PHOTOACOUSTIC RESPONSE OF ABSORBING LIQUID TO MODULATION OF LASER INTENSITY

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Abstract
The photoacoustic response of the absorbing liquid with confined surface to laser pulse with modulated intensity is theoretically studied. The obtained results are compared with experimental data on interaction of pulsed erbium laser radiation (wavelength – 2.94 µm, pulse duration ~ 300 ns) with water.

It was shown in [1-2] that it is possible to monitor the surface movement of absorbing liquid subjected to laser pulse with periodically modulated intensity by registration of arising photoacoustic signal because acoustic modulation period can differ from laser modulation period due to Doppler effect. The movement into the forward direction (collinear with the laser radiation direction) and into the backward direction were observed using this method.

In the present work the behavior of liquid surface irradiated by modulated laser pulse in the confined conditions is considered. In this case the movement into the backward direction is impossible provided the mechanical boundary is rigid enough. However the displacement in the forward direction can be possible in the case of vapor cavity formation. One can estimate the vapor cavity velocity \( V \) with the formula: \( V = \frac{p}{\rho c} \), where \( p \) - pressure in the cavity which depends on the irradiated liquid surface temperature, \( \rho \) and \( c \) are respectively liquid density and sound velocity.

In the case of water and near-critical pressures this velocity can be of order of 10 m/s. During the laser pulse \( \tau \sim 100 \text{ ns} \) the surface displacement \( D \) will be about 1 µm, the correspondent signal time delay \( \Delta t = \frac{D}{c} \) being about 1 ns. For the free surface displacements of the same order of magnitude were detected in [1-2].

When the distribution of laser intensity through the irradiation spot is sufficiently homogeneous (constant) the vapor cavity appearance can result in abrupt pressure rise if the photoacoustic pressure at the boundary is low or comparable with the vapor pressure in the cavity. In the opposite case when the photoacoustic pressure is greater than the critical pressure the vapor cavity should not appear.

This theoretical picture is compared with experimental results obtained in the case of absorbing liquids (water, ethanol) with confined boundary irradiated by erbium laser pulses (\( \tau \sim 300 \text{ ns} \), \( \lambda = 2.94 \text{ µm} \)) with periodically modulated intensity (modulation period ~ 7-8 ns).

It should be mentioned in conclusion that up to now no other experimental investigations of the kind were carried out.

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References
MgZnO AND CdZnO BASED LIGHT EMITTING DIODES

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Abstract. Using pulsed laser deposition, we have grown n-ZnO/p-GaN, n-ZnO/i-ZnO/p-GaN and n-ZnO/n-Mg0.2Zn0.8O/i-Cd0.2Zn0.8O/p-GaN light-emitting diode (LED) heterostructures with peak emission wavelengths of 495, 382 and 465 nm and threshold current densities (used in electroluminescence measurements) of 1.35, 2, and 0.48 A/cm², respectively. Because of the spatial carrier confinement, the n-ZnO/n-Mg0.2Zn0.8O/i-Cd0.2Zn0.8O/p-GaN double heterostructure LED offers a higher electro-luminescence intensity and lower electroluminescence threshold in comparison with the n-ZnO/p-GaN and n-ZnO/i-ZnO/p-GaN LEDs.

1. Introduction
The interest to the problem of creation of various semiconductor devices on the basis of ZnO is caused by that this material possesses a wide spectrum of unique properties. Being the direct gap semiconductor with width of gap energy $E_g=3.37$ eV zinc oxide is the worthy candidate for creation light emitting diodes in near UV spectrum areas. The controlling of band gap width in semiconductors is one of the major problems under production of various heterostructures and designing optoelectronic devices.
The PLD formation of lattice matched Mg$_x$Zn$_{1-x}$O and Cd$_y$Zn$_{1-y}$O films with as much as possible different of the band gap, and also creation light emitting heterostructures n-ZnO/p-GaN, n-ZnO/i-ZnO/p-GaN and n-ZnO/n-Mg$_{0.2}$Zn$_{0.8}$O/i-Cd$_{0.2}$Zn$_{0.8}$O/p-GaN and research of their optical and electric properties were the purposes of the given work.

1.1 Experimental details
Mg$_x$Zn$_{1-x}$O and Cd$_y$Zn$_{1-y}$O films with the 300 nm thickness were received by a pulse laser deposition method from ceramic targets. The ablation of the targets was carried out by the excimer KrF laser with pulse repetition rate of 10 Hz and energy density of 4.2 J/cm$^2$ on a target. The initial vacuum in the working chamber was ~10⁻⁷ Torr. The p-GaN/c-Al$_2$O$_3$ substrates were placed at a 70 mm distance from the target. We used the p-GaN epilayers grown by MOCVD method. The PLD deposition was made at the substrate temperature $T_S=450$ °C and the buffer oxygen pressure of 5 mTorr.

1.2 Results and discussions
It was possible to reach a limit of solubility Mg and Cd in zinc oxide equal $x=0.35$ and $y=0.3$ at using of a method of pulse laser deposition owing to laser plasma non-equilibrium under saving of hexagonal structure of Cd$_y$Zn$_{1-y}$O and Mg$_x$Zn$_{1-x}$O. The mismatch of crystal lattices in a plane of growth didn't exceed 1 % for films Cd$_y$Zn$_{1-y}$O and Mg$_x$Zn$_{1-x}$O up to values $x=0.35$ and $y=0.2$, and breakup of the band gaps thus has made 1.3 eV. Fig.1 represents the transmission spectra $(a)$ and the band gaps $E_g(b)$ of the Cd$_y$Zn$_{1-y}$O and Mg$_x$Zn$_{1-x}$O films as a function of the Cd and Mg concentrations. The roughness of films didn't exceed 2.5 nm for values $x=0-0.27$ and $y=0-0.2$. All parameters of thin films Mg$_x$Zn$_{1-x}$O and Cd$_y$Zn$_{1-y}$O provide possibility to realize high-quality not strained heterostructures Cd$_y$Zn$_{1-y}$O/Mg$_x$Zn$_{1-x}$O for optoelectronic applications in a wide range of values $x$ and $y$ [1,2].

![Fig.1. Transmission spectra $(a)$ and the band gap $E_g(b)$ of the Cd$_y$Zn$_{1-y}$O and Mg$_x$Zn$_{1-x}$O films as a function of the Cd and Mg concentrations.](image-url)
The light emitting diodes on heterojunctions $n$-$\text{ZnO}/p$-$\text{GaN}$, $n$-$\text{ZnO}/i$-$\text{ZnO}/p$-$\text{GaN}$ and $n$-$\text{ZnO}/n$-$\text{Mg}_{0.2}\text{Zn}_{0.8}\text{O}/i$-$\text{Cd}_{0.2}\text{Zn}_{0.8}\text{O}/p$-$\text{GaN}$ heterostructures, with the emission maximum on length of a wave 495 nm, 382 nm, 465 nm and threshold current density $1.35 \text{ A/cm}^2$, $2 \text{ A/cm}^2$ and $0.48 \text{ A/cm}^2$ of the electroluminescence accordingly have been grown up. Fig.2(a,b,c) illustrates the $I$-$V$ characteristics, electroluminescence spectra and working LEDs photo of $n$-$\text{ZnO}/p$-$\text{GaN}$, $n$-$\text{ZnO}/i$-$\text{ZnO}/p$-$\text{GaN}$ and $n$-$\text{ZnO}/n$-$\text{Mg}_{0.2}\text{Zn}_{0.8}\text{O}/i$-$\text{Cd}_{0.2}\text{Zn}_{0.8}\text{O}/p$-$\text{GaN}$ heterojunctions.

The application of narrow band layer $i$-$\text{Cd}_{0.2}\text{Zn}_{0.8}\text{O}$ allowed to realize a light-emitting diode on double heterostructure, which intensity of an electroluminescence larger, because of confinement of charge carriers, and the current density threshold of an electroluminescence lower in comparison with $n$-$\text{ZnO}/p$-$\text{GaN}$ and $n$-$\text{ZnO}/i$-$\text{ZnO}/p$-$\text{GaN}$ light-emitting diodes. Change of Cd content in an active layer will allow to create the radiation sources in dark blue and near UV spectrum range.

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1.4 References


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