BOOK OF ABSTRACTS

INERA WORKSHOP

Transition Metal Oxide Thin Films

Functional Layers in “Smart Windows” and Water Splitting Devices:

Technology and Optoelectronic Properties

September 4 – 6, 2014

Varna, Bulgaria

The INERA Workshop is organized in the frame of the ***FP7 Project REGPOT 316309*** *by the Institute of Solid State Physics and it is dedicated to the 145 anniversary of the Bulgarian Academy of Sciences.*

The topics of the Workshop are planned to cover the field of technology and investigation of thin oxide films as functional layers in electrochromic “Smart windows” and “Water splitting” devices. The event is related to application of novel technologies for preparation of transition metal oxide films and modification of their chromogenic properties for device parameters optimization for possible industrial application.

Topics:

- **Session A**

  Metal oxide films - functional layers in energy efficient devices

- **Session B**

  Photocatalysts and chemical sensing

- **Session C**

  Novel thin film technologies and applications

- **Session D**

  Methods of thin films characterization

Organizing Committee:

Chairperson: Prof. DSc K. Gesheva, kagesh@phys.bas.bg

Secretary: Assoc. Professor Dr A. Szekeres, szekeres@issp.bas.bg

Members:

Assoc. Prof. Dr T. Ivanova, tativan@phys.bas.bg

Assist. Prof. R. Kamburova, radostina.kamburova@gmail.bg

Person to contact:

Prof. DSc K. Gesheva, kagesh@phys.bas.bg

Assoc. Prof. Dr T. Ivanova, tativan@phys.bas.bg

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PROGRAM

Transition Metal Oxide Thin Films – Functional Layers in "Smart Windows" and Water Splitting Devices: Technology and Optoelectronic Properties

September 4 – 6, 2014

Varna, Bulgaria

Thursday, September 4, 2014

Opening Ceremony:	**Kostadinka Gesheva, Introductory remarks**
9:00 - 9:30	**Official opening by Acad. Alexander G. Petrov – INERA Project Coordinator, Director of the Institute of Solid State Physics, Bulgarian Academy of Sciences, Bulgaria**

Session A: Metal oxide films – functional layers in energy efficient devices

Chairperson: Frank Hamelmann

9:30 - 10:10 ***I.A.1***	**Gunnar Niklasson** *(Uppsala University, Sweden)* Functional vanadium oxide thin films: electronic, optical and thermochromic properties
10:10 - 10:30	***Coffee break***
10:30 - 11:10 ***I.A.2***	**Kostadinka Gesheva** *(Central Lab. Solar Energy and New Energy Sources, Bulgarian Academy of Sciences, Bulgaria)* CVD-transition metal oxide coatings for electrochromic “Smart windows”
11:10 - 11:50 ***I.A.3***	**Mariya Aleksandrova** *(Technical University of Sofia, Bulgaria)* Oxide coatings on flexible substrates for electrochromic applications
12:00 - 14:00	***Lunch***

Session A: Metal oxide films - functional layers in energy efficient devices

Chairperson: Kostadinka Gesheva

14:00 - 16:30	**Short presentation of young participants in Poster Session A:** Metal oxide films - functional layers in energy efficient devices
16:30 - 17:00	***Coffee break***
17:00 - 18:30	**Poster Session A:** Metal oxide films - functional layers in energy efficient devices

Friday, September 5, 2014

Session B: Photocatalysts and chemical sensing

Chairperson: Gunnar Niklasson

9:00 - 9:40 **Lars Österlund**
I.B.4 *(Uppsala University, Sweden)*
Photocatalytic oxide films in the built environment

9:40 - 10:20 **Imre Szilágyi**
I.B.5 *(Budapest University of Technology and Economics, Hungary)*
Nanostructured photocatalysts by Atomic Layer Deposition (ALD)

10:20 - 10:40 ***Coffee break***

10:40 - 11:20 **Georgi Popkirov**
I.B.6 *(Central Lab. Solar Energy and New Energy Sources, BAS, Bulgaria)*
Thin oxide films electrodes for photocatalytic water splitting

11:20 - 12:00 **Ion Mihailescu**
I.B.7 *(National Institute for Lasers, Plasma and Radiation Physics, Romania)*
Pulsed laser deposition of thin oxide films for applications in chemical sensing and biological pollution

12:00 - 14:00 ***Lunch***

Session C: Novel thin film technologies and applications

Chairperson: Lars Österlund

14:00 - 14:40 **Frank Hamelmann**
I.C.8 *(Bielefeld University of Applied Sciences, Germany)*
Transparent conductive oxides in thin film photovoltaics

14:40 - 15:20 **Ekaterina Iordanova**
I.C.9 *(Institute of Solid State Physics, BAS, Bulgaria)*
Femtosecond lasers - new technological opportunities

15:20 – 15:40 ***Coffee break***

15:40 - 18:00 **Short presentation of young participants in Poster Sessions B, C:**
Session B: Photocatalysts, chemical sensing
Session C: Novel thin film technologies and applications

18:00 - 19:30 **Poster Sessions B and C**

Saturday, September 6, 2014

Session D: Methods of thin films characterization

Chairperson: Georgi Popkirov

9:30 - 10:10 **Victor Ivanov**
I.D.10 *(University of Sofia, Bulgaria)*
Modern applications of Raman Spectroscopy

10:10 - 10:50 **Anna Szekeres**
I.D.11 *(Institute of Solid State Physics, BAS, Bulgaria)*
Application of Ellipsometry in studies of metal oxide thin films

10:50 - 12:00 **Students awards; Closing ceremony**

12:00 - 14:00 ***Lunch***

14:00 – 19:00 ***Free time, Social event***

19:00 **Gala Dinner**

INVITED LECTURES

I.A.1

Thermochromic Vanadium Oxide Thin Films: Electronic and Optical Properties

***G. A. Niklasson**, S.-Y. Li and C.G. Granqvist*

Department of Engineering Sciences, The Ångström Laboratory, Uppsala University
P.O. Box 534, SE-75121 Uppsala, Sweden
Corresponding author: gunnar.niklasson@angstrom.uu.se

Vanadium dioxide, VO_2, is a widely studied thermochromic material with potential applications in energy efficient window technology. It undergoes a first-order metal-to-insulator transition, accompanied by a crystal structure transformation from monoclinic to tetragonal rutile, at a critical temperature of 68^{o}C. Below this temperature, VO_2 is semiconducting and infrared transmitting whereas it is metallic and infrared reflecting above the transition temperature.

However, in order to achieve significant thermochromic switching, the luminous transmittance of thin films will be less than 0.5. Here we report on recent research to improve the luminous transmittance as well as the transmittance change at the transition temperature.

We systematically evaluate the effect of antireflection coatings, doping with Mg and the performance of coatings comprising thermochromic nanoparticles in a transparent matrix. The last option is shown to give the best performance and holds great promise for practical applications.

I.A.2

APCVD Transition Metal Oxides – Functional Layers in “Smart Windows”

***K. A. Gesheva*, T. M. Ivanova and G. K. Bodurov**

Central Laboratory of Solar Energy and New Energy Sources, Bulgarian Academy of Sciences,
Blvd. “Tzarigradsko chausses” 72, 1784 Sofia, Bulgaria
Corresponding author: kagesh@phys.bas.bg

Transition metal oxides (TMO) exhibit electrochromic effect, under a small voltage they change their optical transmittance from transparent to collored (absorbing) state. The individual material can manifest its electrochromic properties only when it is a part of electrochromic (EC) stack system - EC device. Smart window is a device controlling the energy of solar flux entering the building or car and make the interiors comfortable and at the same time energy utilization more effective.

We have optimized atmospheric pressure chemical vapor deposition (APCVD) utilizing metal hexacarbonyls as precursors for deposition of numerous transition metal oxide films on conductive glass. Under a voltage applied the films color in a different colors depending on the absorption nature of the film material, and bleaches up, after voltage polarity change. Coloring effect is a result of electrical charge transfer in the system, it intercalates in film structure, and deintercalate out of it.

Recently the efforts of the material researchers in this field are directed to price decreasing. We consider APCVD as promising due to the fact that utilizing atmospheric pressure process it permits a flow-through large-scale production.

The presentation deals with the optimization of a device, based on working electrode of WO_3-MoO_3 mixed films. The extensive research done on the film materials leads to conclusion, that WO_3-MoO_3 mixed structure combines the excellent electrochromic performance of WO_3 and higher growth-rate of MoO_3. Colour efficiency approaching 200 cm^2/C combined with optical modulation between 65-70% are practically acceptable electrochromic performance characteristics.

To respond to the price lowering, the expensive hexacarbonyl precursor in on a way to be replaced with acetylacetonates. We have started knowing this precursor in our attemps to fabricate mixed $W_xV_{1-x}O_3$ films. The films possess excellent surface coverage and high-growth-rate. These technological experiments are our start to the promissing, largely studied recently thermochromic VO_2. Results on APCVD deposition process, employing Vanadyl Acetylacetonate as a precursor will be presented.

I.A.3

Oxide Coatings on Flexible Substrates for Electrochromic Applications

M. Aleksandrova

Technical University of Sofia, Bulgaria, Department of Microelectronics, Sofia 1000, Kliment Ohridski blvd, 8, bl. 1
Corresponding author: m_aleksandrova@tu-sofia.bg

Modern microelectronic devices consist of coatings, having variety of functionalities. One of the most studied classes of materials is metal oxides. There are different metal oxide films in the devices construction, such as electrodes, charge injecting and transporting coatings, electrochromic coatings for displays or "smart" windows applications, gas sensitive, etc.

This paper aims to describe state-of-the-art technology for conductive oxide films on flexible substrates, applied in the electrochromic devices. Although many deposition techniques for production of such films have been developed (for example chemical vapor deposition (CVD), spray pyrolysis and electrodeposition), there some of the achievements in the field of physical vapor deposition (PVD) on low-cost, but easy damageable flexible substrates are discussed.

The focus is put on the transparent electrodes for electrochromic devices. Possible approaches for keeping the deposition temperature as low as possible to prevent substrate melting are compared. Attention is paid to some critical issues, such as electrode films' adhesion, their electro-optical parameters (sheet resistance, transparency in the visible range) and patterning ability. The influence of the deposition modes and film thickness on the electrical, optical and mechanical properties is also commented.

I.B.4

Photocatalytic Oxide Films in the Built Environment

L. Österlund

Dep. Engineering Sciences, The Ångström Laboratory, Uppsala University, SE-751 21
Uppsala, Sweden
Corresponding author: lars.osterlund@angstrom.uu.se

The possibility to increase human comfort in buildings is a powerful driving force for the introduction of new technology. Among other things our sense of comfort depends on air quality, temperature, lighting level, and the possibility of having visual contact between indoors and outdoors. Indeed there is an intimate connection between energy, comfort, and health issues in the built environment, leading to a need for intelligent building materials and green architecture. In this lecture the focus will be on photocatalytic materials, mainly transition metal oxides such as TiO_2. These materials can be applied as coatings, filters, and be embedded in building materials to provide self-cleaning, antibacterial, air cleaning, deodorizing, and water cleaning functions utilizing either solar light or artificial illumination sources – either already present in buildings, or by purposefully designed luminaries. Huge improvements in indoor comfort can thus be made, and also alleviate negative health effects associated with buildings, such as the sick-house syndrome. At the same time maintenance costs can be largely reduced.

The basic mechanism responsible for the function of these photocatalytic materials will be described from a surface science perspective [1]. Photocatalytic oxides can be chemical modified by changing their acid-base surface properties, which can be used to overcome deactivation problems commonly encountered for TiO_2 [2, 3]. The oxide surfaces can be rendered very wettable (super-hydrophilic) and a favorable decontamination process based on film flow arises [4]. The mechanism underlying this wetting behavior is fairly well understood on TiO_2, and is reviewed here. In addition, the wetting properties oxides can be tailored by surface chemical modifications and made e.g. oleophobic [5]. Self-cleaning surfaces using this principle have been fabricated by coating nanostructured thin films of TiO_2 on various substrates. This type of coating can be made transparent and incorporated in e.g. anti-reflective and anti-bacterial coatings, etc. A commercial application of super-hydrophilic TiO_2 thin films is the self-cleaning, or easy-clean windows, which has a thin, transparent film of TiO_2 deposited on their exterior surfaces, and which today is manufactured by all major glass manufacturing companies. Other examples given in the lecture include photocatalytic cement, which today is considered as air purifying building elements both indoor and outdoor.

References

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[3]. L. Österlund, *Trends Photochem. Photobiol.* 12 (2010) 53; L. Österlund, *Solid State Phenom.* 162 (2010); L. Österlund, In: *On Solar Hydrogen and Nanotechnology* (Ed.) L. Vayssieres (Wiley & Sons, Singapore, 2009).
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I.B.5

Nanostructured Photocatalysts Prepared by Atomic Layer Deposition (ALD)

I. M. Szilágyi[1,2]

[1]*Budapest University of Technology and Economics, Department of Inorganic and Analytical Chemistry, Budapest, Szent Gellért tér 4., H-1111, Hungary*
[2]*MTA-BME Technical Analytical Chemistry Research Group, Budapest, Szent Gellért tér 4., H-1111, Hungary*
Corresponding author: imre.szilagyi@mail.bme.hu

Semiconductor oxides are widely used photocatalysts to decompose organic contaminations with solar energy. The activity of these photocatalysts can be further improved by doping them with heteroatoms, by making composites of them with other semiconductor oxide materials, noble metal nanoparticles, organic dyes and other organic absorbers, or by increasing their specific surface using highly structured substrates.

Atomic layer deposition (ALD) is an outstanding tool, by which all of these materials can be prepared. ALD is a thin film deposition method, where the thickness of films can be controlled truly atom by atom. ALD is based on successive, alternating surface controlled reactions from the gas phase to produce highly conformal and uniform thin films with thickness control of sub-nanometer precision. Thus, ALD provides new strategies in modifying the properties of nanoscaled materials and new synthetic routes to novel nanostructures.

In the presentation, several examples will be shown about how various nanostructured photocatalysts can be obtained by ALD. Sulfur and fluorine doped TiO_2 thin films deposited by ALD were active photocatalysts in visible light. By combining electrospinning and ALD, WO_3/TiO_2, ZnO/TiO_2 and TiO_2/ZnO core/shell Vis or UV active nanofiber photocatalysts were prepared. $CoFe_2O_4$ and Fe_2O_3 loaded TiO_2 nanotubes had magnetic and photocatalytic properties. High surface area Al_2O_3 membranes, Ni nanowires, porous steel fiber matrix coated with TiO_2 all had significantly enhanced photocatalytic properties.

Photocatalysts based on biological substrates can be also manufactured by ALD, e.g. cellulose fibers coated with TiO_2 nanofilms and iridium nanoparticles, or TiO_2 coated lotus leaves with both superhyrophobic and photocatalytic activities. C_{60}/TiO_2; $CNT/ZnO/TiO_2$ and $CNT/TiO_2/ZnO$ composites are examples for ALD prepared carbon nanostructure based photocatalysts.

I.B.6

Thin Film Oxide Electrodes for Photocatalytic Water Splitting

G. Popkirov

Central Laboratory of Solar Energy and New Energy Sources, Bulgarian Academy of Sciences,
Blvd. "Tzarigradsko chaussee" 72, 1784 Sofia, Bulgaria
Corresponding author: popkirov@yahoo.com

The lecture will present the current state of research activities and results in the effort to obtain efficient photocatalytic splitting of water, being one of the promising methods to convert solar energy into the chemical energy of the hydrogen fuel. The lecture will start with an introduction to the hydrogen economics: hydrogen is storable, transportable and can be converted into electricity using fuel cells. Hydrogen is an important feedstock in the modern chemical industry, it could be used further for methanol synthesis and thus in an energy cycle involving carbon dioxide recycling.

The lecture will further show how solar energy can be converted into the energy of the hydrogen fuel either by *thermal* or *photonic* processes. Photovoltaic cells connected to an electrolyzer and photobiological systems for hydrogen production using solar energy assisted water splitting will be shortly presented.

As a main topic of the lecture, recent research of photoelectrochemical cells and results obtained using semiconductor photoelectrodes, functionalized with H_2- and O_2-evolution catalysts for photoelectrochemical hydrogen production will be presented and discussed.

I.B.7

Pulsed Laser Deposition of Thin Oxide Films for Applications to Chemical Sensing and Biological Pollution

I. N. Mihailescu ***and C. Ristoscu***

National Institute for Lasers, Plasma and Radiation Physics, Lasers Department, 409
Atomistilor Street, Magurele, Romania
Corresponding author: ion.mihailescu@inflpr.ro

Titanium dioxide is cheap, non-toxic, and stable to chemical corrosion and photocorrosion and has excellent photocatalytic activity. It has been therefore widely studied for the past few decades as a promising material for environmental protection, self-cleaning, deodorizing and sterilizing applications.

Simple TiO_2 or doped TiO_2/ZrO_2 films were obtained by Pulsed Laser Deposition method under different synthesis conditions. The onset of absorption spectra was red shifted for the films obtained in N_2 containing gas mixtures, while a broad absorption in visible was observed in the case of films deposited in CH_4 atmosphere. The influence of synthesis conditions on the efficiency of nitrogen incorporation in the presence of double doping agents (N_2/CH_4) was studied. The presence of low content of CH_4 in deposition ambiance (10:1 N_2/CH_4) boosted the formation of O-Ti-N fragments in metal oxide matrix as evidenced from the remarkable appearance of Ti2p3/2 (Eb=457.5 eV) and N1s (Eb=395.8 eV) peaks in XPS spectra. The presence of O-Ti-N bonds corresponded to the highest photocatalytic performance. XPS spectra of the samples obtained in N_2/CH_4 gas mixtures evidenced a more effective incorporation of nitrogen in the structure due to oxygen deficiency.

The nitrogen incorporation induced the traps for charges photogenerated by light and leaded to the improvement in photocatalytic reduction of toxic Cr(VI) to Cr(III) under UV light. The TiO_2 band-gap narrowing is mandatory for extending the photocatalytic action to visible light. Other factors such as an effective trapping of photogenerated charge carriers, adsorption/desorption of reaction components and appropriate redox couples could crucially influence the recombination rate of an electron-hole pair.

I.C.8

Doped Zinc Oxide as Transparent Conductive Oxide in Thin Film Photovoltaics

***F. U. Hamelmann* and J. Weicht**

Bielefeld University of Applied Sciences, Ringstr. 94, D-32427 Minden, Germany
Corresponding author: frank.hamelmann@fh-bielefeld.de

Doped zinc oxide films are of high interest in thin film solar cell technology for application as transparent conducting oxide. Zinc Oxide is a wide band gap semiconductor, it can be doped with a variety of elements, commonly used are Boron, Aluminium and Gallium. The doping level controls the transparency and the conductivity of the films. For the application in thin film silicon solar cells it is necessary to get a rough surface with a controlled RMS-roughness and surface texture. This property is important to achieve a good light scattering, low optical losses due to reflection at the material interfaces combined with good electrical properties of the film and the interfaces.

Two different methods for deposition with the potential for large area (>1m^2) and high volume production were used and compared. Low Pressure CVD is used to deposit boron doped zinc oxide with a native pyramid shaped surface structure that allows very good light scattering for thin film solar cells. Due to the nano-porous bulk material, the films are sensitive to moisture. A good encapsulation of the solar modules is required.

Sputtering of aluminium doped zinc oxide is an alternative technology for high quality transparent conductive oxides in thin film solar cells. The films are growing compact and do not show sensitivity to humidity, but they are smooth and need a post-deposition treatment to enable light scattering. This is realised by a short wet chemical etching step in low concentrated hydrochloric acid. Craters with a tuneable size are the result.

Details of the deposition processes are given, as well as a comparison of the material properties with respect to the electrical and optical characteristics and the long term stability of the films. In addition, a new method for the analysis of porous polycrystalline dielectric thin films [1] and new results about the Schottky barrier between doped zinc oxide and silicon [2] are given.

References

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[2]. A. N. Corpus-Mendoza, M. M. De Souza, F. Hamelmann, “Transport Mechanisms and effective Schottky barrier height of ZnO/a-Si:H and ZnO/µc-Si:H heterojunction solar cells”, J Appl. Phys. 114 (**2013**), 184505.

I.C.9

Femtosecond Lasers – New Technological Opportunities

G. Yankov, E. Iordanova, R. Barbucha, M. Kocik, T. Petrov and M. Grozeva

Institute of Solid State Physics, Bulgarian Academy of Science, Sofia, Bulgaria
Corresponding author: eiordanova@issp.bas.bg

The ability to configure 3-dimensional characteristics from the micron- to nanoscale has huge potential to impact many fields, including micromachining, chemical engineering biomedicine and biotechnologies.

Nanostructures and nanosystems take advantage not only of the small dimensions of the objects but of the specific way of interaction between nano objects. The understanding of internal dynamics on femtosecond time scale is utterly important and requires advanced measurement techniques. Here, comes the role of ultra short laser pulses, with durations approaching the timescales of fundamental atomic and molecular processes, they are applicable in a wide range of scientific disciplines.

The development of lasers with pulse lengths of the order of femtosecond laser sources allows better observation of ultrafast processes and time-resolved measurements. They deliver energy so quickly that new processes and investigations are possible. The short pulse duration allows probing delicate living structures without destroying them. The material and surface modifications (such as hole drilling, surface cleaning and removal of defects, and photolithographic mask repair), on the nanoscale can be done with precisely controllable heat effects.

I.D.10

Modern Applications of Raman Spectroscopy

V. G. Ivanov

University of Sofia, Faculty of Physics, Blvd. James Bourchier 5, Sofia 1164, Bulgaria
Corresponding author: vd_bsc@phys.uni-sofia.bg

Raman spectroscopy (RS) is a universal characterization method in material science, which is based on optical detection of elementary excitations in matter. Most of the RS applications relay on investigation of phonons but it can equally be used for sensing of several other types of excitations, like magnons, crystal-field transitions, plasmons, and the superconducting gap in superconductors.

RS is unique among other characterization techniques by being informative for the long-range crystalline order through the polarization selection rules as well as to the local atomic coordination through the frequency shifts of the scattered photons. In this aspect RS is a valuable supplement to the traditional structural methods like X-ray and neutron diffraction, which are sensitive to the long-range order only or to the purely local probes as nuclear magnetic resonance, Mossbauer spectroscopy and electronic paramagnetic resonance.

The lecture is intended to a broad audience and provides an introduction to the physical basics and modern applications of Raman spectroscopy in material science. Several examples are given for RS characterization of complex oxides, carbon allotropes, and polymers. Special attention is paid to the modern forms of Raman spectroscopy like Surface- and Tip-Enhanced Raman Spectroscopy (SERS and TERS).

I.D.11

Application of Ellipsometry in Studies of Metal Oxide Thin Films

A. Szekeres

Institute of Solid State Physics, Bulgarian Academy of Science, Sofia, Bulgaria
Corresponding author: szekeres@issp.bas.bg

Ellipsometry is a powerful tool for thin film characterization, largely utilized worldwide. This optical technique is very sensitive to any small changes in the film structure, composition, thickness, and thus to changes in the resulting properties. Highly valuable information offers the spectral ellipsometry, utilized in wide spectral range of light starting from the ultraviolet up to the far infrared region.

In this lecture examples for application of spectroscopic ellipsometry in material research will be presented, most specifically metal oxide thin films. These oxides are important materials not only from the scientific point of view but for application in different optoelectronic devices.

We report results from studying the optical properties of semiconductor oxides, such as TiO_2, ZnO, MoO_3, WO_3, as well as mixed structures on their basis. The variation in optical parameters are considered and correlated to the technological parameters of films preparation.

POSTERS

Session A

Metal Oxide Films – Functional Layers in Energy Efficient Devices

A.1

Electrochromic Properties in Li^+-Intercalated Amorphous Titanium Oxide a-TiO_{2-x} and Tungsten Oxide a-WO_{3-x} $_{(0 \leq x \leq 1)}$ Thin Films

***C. A. Triana Estupiñan*, C.G. Granqvist and G.A. Niklasson**

Department of Engineering Sciences, The Ångström Laboratory, Uppsala University, P.O. Box 534, SE-751 21 Uppsala, Sweden
Corresponding author: carlos.triana@angstrom.uu.se

Amorphous titanium oxide a-TiO_{2-x} and tungsten oxide a-WO_{3-x}, are ones of the most important materials for electrochromic coatings in smart window applications, and promising switching materials with a wide range of technical applications. Thin films of these materials exhibit optical modulation from bleached to colored states upon ion-e^- intercalation by application of a low voltage, thereby offering good performance for integration in multilayer devices and information displays.

In this work, we report on a comprehensive study on the electrochromic properties of a-TiO_{2-x} and a-WO_{3-x} thin films under Li^+-ion-e^- intercalation/deintercalation. Stoichiometric and oxygen-deficient thin films were deposited by reactive DC magnetron sputtering onto unheated glass substrates pre-coated with transparent conductive indium-tin oxide. Depositions were carried out at the same values of pressure, power and argon flow ratio, but using different oxygen flow ratios. Film thicknesses lay in the range 300–320 nm, and XRD analysis confirmed the amorphous phase.

Subsequent electrochemical Li^+-ion-e^- intercalation/deintercalation in the as-deposited films using 1 M $LiClO_4$ in propylene carbonate, were performed by positioning the a-TiO_{2-x} and a-WO_{3-x} thin films in an electrochemical tree-electrode arrangement. Optical characterization of films in their as-deposited and Li^+-ion intercalated states were performed by transmittance and reflectance measurements in the UV/Vis/NIR energy range of 0.5–4.5 eV. Cyclic voltammetry demonstrated good optical modulation, coloration efficiency and charge capacity upon ion intercalation/deintercalation.

Our results indicated that carefully chosen deposition parameters, especially oxygen contents, are beneficial for achieving good electrochromic properties of the films. An analysis of the complex dielectric function as a function of phonon energy showed a variation of the optical properties consistent with absorption phenomena.

Durability of Thermochromic VO_2 Thin Films under Heating and Humidity

***Y.-Xia Ji*, S.-Yi Li, G. A. Niklasson and C. G. Granqvist**

Department of Engineering Sciences, The Ångström Laboratory, Uppsala University, P.O. Box 534, SE-751 21 Uppsala, Sweden
Corresponding author: yuxia.ji@angstrom.uu.se

The thermochromic (TC) material VO_2 has been discussed as an adaptive coating for spectrally selective windows for a very long time, but it is still fumbling on the way to practical applications.

One of the critical points is that the structure of VO_2 is not thermodynamically stable and may be oxidized and form non-thermochromic V_2O_5. Exposure of VO_2 to high temperature and air humidity can cause the coating to be damaged. This has limited VO_2 to be used as a window coating since practical TC windows obviously require long-term durability.

An explorative study on sputter-deposited thermochromic VO_2 films with Al oxide top coating was therefore performed. The films were exposed to heat treatment under dry air and high humidity conditions. The ambient conditions were harsh and 80-nm-thick VO_2 films rapidly converted to non-TC V_2O_5 under the chosen conditions. It was found that a 30-nm-thick sputter-deposited Al oxide top coating provided good protection and delayed the oxidation for more than one day upon heating in dry air at 300°C and that protection occurred for several days at 95 % relative humidity and 60°C. The thickness of the Al oxide was important and, expectedly, increased thickness yielded enhanced protection.

The results demonstrate the importance of protective layer of thermochromic windows for practical application as well as for other technical applications.

Optical Properties of Complex Transition Metal Oxides Grown by Combinatorial PLD Technique

G. Popescu-Pelin[1,3]***, D. Craciun***[1]***, V. Craciun***[1]***, G. Socol***[1]***, N. Stefan***[1]***, A. C. Galca*** [2]***, N. Becherescu***[3] ***and I. N. Mihailescu***[1]

[1]*National Institute for Lasers, Plasma and Radiation Physics, Magurele, Ilfov, Romania*
[2]*National Institute of Materials Physics, Magurele, Ilfov, Romania*
[3]*Faculty of Physics, University of Bucharest, Magurele, Ilfov, Romania*
Corresponding author: gianina.popescu@inflpr.ro

Coatings of various transition metal oxides were grown by Combinatorial Pulsed Laser Deposition (CPLD) technique to evaluate the structure, surface morphology, composition and optical properties with respect to their emissivity for outer space radiator applications. CPLD is a powerful, rapid and inexpensive technique used to obtain data libraries of complex multicomponent compounds.

In our experiments HfO_2 with TiO_2 and ZrO_2 with HfO_2 were mixed in order to select the composition ratio with the best combination of high emissivity, thermal stability and thermal shock resistance properties. Composite mixtures of transition metal oxides were deposited on (100) Si wafers and glass slides into oxygen atmosphere of 10 Pa. Targets-substrate separation distance was 5 cm while the distance between the laser spots was set at 30 mm. During the laser ablation, the substrates were heated at 400 °C to improve the crystallinity of combinatorial oxide thin films.

X-ray reflectivity (XRR), x-ray diffraction (XRD), spectroscopic ellipsometry (SE), optical spectrophotometry, Rutherford backscattering spectrometry (RBS) and X-ray fluorescence (XRF) investigations were performed to identify the optimal composition that maximizes the optical properties in respect with the targeted application.

A.4

Improved Electrochromic Durability of Nickel Oxide by Introducing Iridium

***R.-T. Wen*[1]*, G. A. Niklasson*[1] *and C. G. Granqvist*[1]

[1]*Department of Engineering Sciences, The Ångström Laboratory, Uppsala University, P.O. Box 534, SE-751 21 Uppsala, Sweden*
Corresponding author: Ruitao.Wen@angstrom.uu.se

Nickel oxide and iridium oxide are well-known anodic electrochromic (EC) materials. A typical application for EC thin films is in smart windows, which can be used to decrease energy consumption and eliminate glare in buildings and automobiles.

A large amount of work has been done on nickel oxide films in order to meet the demands for smart window applications, such as compatibility with cathodic EC films and electrolytes, long-term cycling durability and large optical modulation. However, pure nickel oxide films exhibit poor long-term cycling durability and iridium oxide is considered superior because of its excellent electrochemical stability, chemical resistance and EC cycling speed, but an obvious limitation for iridium oxide is its limited global abundance and high price.

The aim of our present work is to improve nickel oxide based anodic EC layers for smart windows applications by doping small amounts of iridium into the nickel oxide lattice. Our films were prepared by reactive (direct current) DC magnetron sputtering in argon and oxygen. Structure, composition and chemical bonding of iridium doped nickel oxide films were determined by X-ray Diffraction (XRD), Rutherford backscattering spectrometry (RBS) and X-ray photoelectron spectroscopy (XPS), respectively. Optical modulation, durability and cyclic voltammetry were recorded and compared with corresponding data for pure nickel oxide and iridium oxide thin films with the object of optimizing the anodic EC layer for smart windows.

Sprayed Electrochromic Devices for Application as Smart Glazing in Buildings

G. Bodurov[1,3,*]***, Y. E. Romanyuk***[1]***, A. N. Tiwari***[1]***, E. Jung***[2]***, D. Nadargi***[2]***, M. Koebel***[2]***, T. Ivanova***[3] ***and K. Gesheva***[3]

[1] *Laboratory for Thin Films and Photovoltaics at EMPA, Ueberlandstrasse 129*
CH-8600 Dübendorf, Switzerland
[2]*Laboratory for Building Science and Technology at EMPA, Ueberlandstrasse 129*
CH-8600 Dübendorf, Switzerland
[3] *Central Laboratory of Solar Energy and New Energy Sources at the Bulgarian Academy of Sciences, 72 Tsarigradsko shausee Blvd., 1784 Sofia, Bulgaria*
Corresponding author: Joro.bodurov@yahoo.com

Thin films of WO_3 deposited by ultrasonic spray pyrolysis and sol-gel dip coating are promising low coast materials for application as functional electrodes in electrochromic devices (ECDs). Numerous studies have been conducted on sprayed and sol-gel WO_3 films, but only few are related to construction and characterization of ECDs, which is mostly due to inherent challenges of the spray pyrolysis and sol-gel dip coating methods, such as the solution stability, the need of post-treatment and film uniformity leading to complex control on the technological parameters.

Herein we present results on the deposition and characterization of WO_3 thin layers deposited by sol-gel and ultrasonic spray pyrolysis methods from poly-tungstic acid precursor solutions, and subjected to a high temperature annealing at 450°C.Average film thickness of 300 nm was tailored. XRD measurements confirmed the desired WO_3polycrystalline phase, whereas UV-Vis spectrophotometry was used to determine transmittance and reflectance of the films. SEM and AFM measurements were conducted for characterization of the film surface morphology. FTIR measurements confirmed the results from the XRD.

Electrochromic devices were fabricated in the configuration Glass/FTO/ WO_3/Electrolyte/Pt/FTO/Glass, with liquid and gel electrolytes. The EC performance of sprayed and sol-gel-based devices was compared in terms of their optical switching modulation, transmittance/reflectance, response time, and coloration efficiency. Our studies showed that electrochromic device with sol-gel WO_3 functional electrode and liquid electrolyte has the highest coloration efficiency of 41 cm^2 C^{-1} for 633 nm, combined with the best charge capacity compared to the other tested devices.

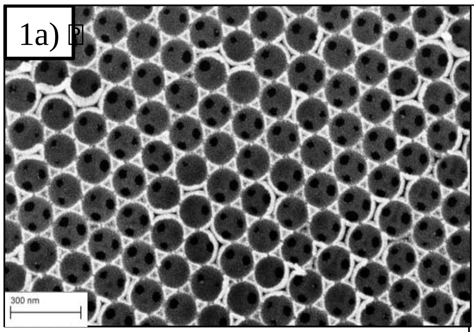
Versatile Multi-Layered Metal-Oxide Inverse Opal Fabrication for Photocatalytic Applications

***D. Lebrun*[1*], *L. Österlund*[1], *G. Niklasson*[1] *and V. Kapaklis*[2]**

[1]*Dept of Engineering Sciences, Uppsala University, Uppsala, SWEDEN*
[2]*Dept of Physics and Astronomy, Uppsala University, Uppsala, SWEDEN*
Corresponding author: dele@angstrom.uu.se

Inverse opals are photonic band gap structures with a close-packed periodicity. The photonic band gap is a forbidden energy range for the light. Inverse opals have therefore been studied for a wide range of applications, as for example photocatalysis. Matching the photonic band gap to the electronic band gap allow an increase in the electron-hole pair formation (indirect band gap materials) and a quenching of the recombination rate (direct band gap). Also, in the vicinity of the bands, the light is slowing down, increasing the photon absorption within the material. Multi-layered structures are versatile: different thicknesses of metal-oxides can be deposited and therefore change the photonic band gap (*see Fig. 1*), but also nano-particles can be integrated between layers (plasmonic effect) or at the surface (higher surface area).

By controlling periodicity, materials and growth method, it is possible to tune the photonic band gap. However, these structures are sensitive to defects and their fabrication is not straightforward. We propose a three-step fabrication method: self-assembly by convective evaporation of polystyrene beads into opal structures; atomic layer deposition (ALD) of metal oxides (Al_2O_3, ZnO, TiO_2 and Fe_2O_3); annealing and ion milling to form the inverse opal structure. ALD was performed either directly on the opal structure or on the inverse opal structure. Ar-ion milling was used to access the hollow structure without damaging the sample. Our opals and inverse opals can be created on various substrates such as quartz, indium tin oxide and flexible plastic film. We characterized the structures using optical spectroscopy (UV-VIS), X-ray spectroscopy, electron microscopy, and profilometry. A summary of our preparation techniques and systematic analysis will be presented.



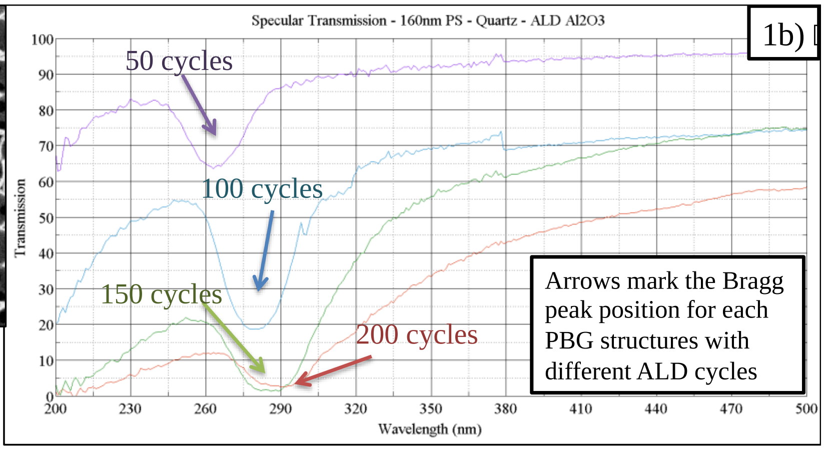


Fig.1 *a)* Scanning electron microscopy of Al_2O_3 inverse opal, *b)* UV-VIS transmission spectra of Al_2O_3 inverse opal with different atomic layer deposition cycles

Doping of Calcium Phosphate with ZrO_2 by Pulsed Laser Transfer: Composition, Structure, Morphology and Potential Applications

***M. Sopronyi*[1], *C.Ristoscu*[1], *I. N. Mihailescu*[1], *E. Palcevskis*[2] *and A. Dindune*[2]**

[1]*National Institute for Lasers, Plasma and Radiation Physics, Lasers Department, 409 Atomistilor Street, Magurele, Romania*
[2]*Institute of Inorganic Chemistry, Riga Technical University, Miera iela 34, 2169 Salaspils, Latvia*
Corresponding author: mihai.sopronyi@inflpr.ro

Calcium phosphates (CaPs) focused nowadays a large research interest because their similitude to the vertebrate system of many animals including humans. In particular hydroxyapatite (HA) represents (65-75% wt) of the inorganic part of human bone manly depending on sex and age. Unfortunately thin films of CaPs are very fragile because they easily brittle under stress. For practical use as coatings for bone implants, CaPs thin films should therefore doped with additives which strengthen implants toughness.

We herewith report on Ce stabilized ZrO_2 doped HA thin films synthesized by pulsed laser deposition (PLD) onto Al_2O_3 substrates. For deposition in form of thin films, we used an excimer laser source (λ=248 nm, $\tau \approx$ 25 ns). The depositions were performed in a 50 Pa water vapor flux and the substrates were softly heated to promote crystallization. SEM, TEM and FTIR analyses of deposited films were carried out in order to check up the composition, structure and morphology of obtained nanostructures. After in vitro studies, the thin films were found biocompatible, in direct correlation with substrates porosity.

A.8

Incorporation of Nitrogen into TiO_2 Thin Films during PVD Processes

I. Asenova[1,2], D. Manova[2] and S. Mändl [2]

[1]National Institute[1]Sofia University "St. Kliment Ohridski", Faculty of Physics, 5 James Bourchier Blvd, 1164 Sofia, Bulgaria
[2]Leibniz-Institute für Oberflächenmodifizierung, 15 Permoserstra□e, D-04318 Leipzig, Germany
Corresponding author: iasenova@phys.uni-sofia.bg

Titanium dioxide is well known as a photoactive material, either as a photocatalyst under UV irradiation or exhibiting superhydrophilic, self-cleaning surface. While TiO_2 thin films can be produced on nearly any material using ion assisted physical vapour deposition processes at low temperatures, the band gap is more than 3 eV (depending on the polymorph) necessitating UV radiation for activation.

One possibility of reducing the band gap is doping or alloying with nitrogen readily accessible during PVD processes. However, the incorporation of nitrogen into the growing film is much smaller than for oxygen due to the higher reactivity of the latter. In this investigation, a series of deposition experiments employing a titanium vacuum arc with gas backfill ranging from pure oxygen to pure nitrogen is performed.

The resulting films are characterized for chemical composition, phase composition, optical properties and hydrophilicity to determine a correlation between gas composition and thin film properties.

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Session B

Photocatalysts and Chemical Sensing

B.1

Enhancing the Photocatalytic Activity of Nanocrystalline Anatase TiO_2 Thin Films by Fine-Tuning the <001> Orientation

B. Stefanov, C.-Göran Granqvist and L. Österlund

Department of Engineering Sciences, The Ångström Laboratory, Uppsala University,
P.O. Box 534, SE-751 21 Uppsala, Sweden
Corresponding author: lars.osterlund@angstrom.uu.se

Anatase TiO_2 thin films were deposited by reactive DC magnetron sputtering in Ar/O_2 atmosphere and were characterized using Rietveld refined grazing incidence X-ray diffraction, atomic force microscopy, spectrophotometry and surface profilometry.

Upon heat-treatment for 1 h at 500ºC, the as-deposited amorphous films were found to crystallize into a polycrystalline anatase phase with grain size between 18 and 26 nm. By varying the partial O_2 pressure in the deposition chamber, the degree of orientation of the grains in the film could be systematically varied with preferred <001> orientation changing between 12 and 38%.

Photocatalytic degradation of methylene blue dye under UV illumination shows that the photooxidation rate correlates with the degree of <001> orientation of the films.

B.2

Porous Nickel Oxide Sensor for Detecting Formaldehyde

***U. Cindemir**, Z. Topalian, L. Österlund, C.-Göran Granqvist and G. A. Niklasson*

Uppsala University,P.O. Box 534, SE-751 21 Uppsala, Sweden
Corresponding author: umut.cindemir@angstrom.uu.se

Formaldehyde is a volatile organic compound, which is a harmful indoor pollutant, contributing to the sick building syndrome (SBS). In addition to SBS, formaldehyde is also considered to be carcinogenic. Thus, monitoring it indoors is of great importance.

Advanced gas deposition has here been used to fabricate highly porous nickel oxide (NiO) thin films for formaldehyde sensing. The films were deposited on Al_2O_3 substrates with prefabricated comb-structured electrodes, and a resistive heater at the opposite face. The morphology of the films was investigated with scanning electron microscopy, and the porosity was determined by nitrogen adsorption isotherms with the Brunauer-Emmett-Teller method. The particle size was found to be less than 10 nm, as determined by x-ray diffraction. Chemical surface composition was measured by X-ray photoelectron spectroscopy.

Gas sensing measurements were done in a total gas flow rate of 200 ml/min. Sensor resistances were recorded with formaldehyde diluted in synthetic air at formaldehyde concentrations of 50 ppm, 25 ppm, 10 ppm and 5 ppm. The measurements showed a response time of 2.5 minutes and saturation time around 20 minutes at 50 ppm. After three cycles, at 150 °C, NiO films showed resistance increases from 1.2% to 3.8%, for 5 ppm and 50 ppm of formaldehyde, respectively. The resistance drift is defined as the ratio of the time averaged resistance in synthetic air, after and before the three cycles of gas exposure, and the drift values varied between 2.9% and 6.4% at different gas concentrations.

An Application of Silicon Nanocrystals in UV Sensors

V. Dzhurkov^{1*}***, A. Arias***^{2}***, D. Nesheva***^{1}***, M. Curiel***^{2}***, N. Nedev***^{2}***, E. Manolov***^{1}***, B. Valdez***^{2}***,***
R. Herrera^{2}***, O. Perez***^{2}***, O. Contreras***^{3}***, D. Mateos***^{2} ***and J.M. Siqueiros***^{3}

^{1}*Institute of Solid State Physics, Bulgarian Academy of Sciences,72 Tzarigradsko Chaussee Blvd., 1784 Sofia, Bulgaria*
^{2}*Institute of Engineering, Autonomous University of Baja California, Benito Juarez Blvd. s/n, C.P.21280, Mexicali, B.C,Mexico*
^{3}*Centro de Nanociencias y Nanotecnología, Universidad Nacional Autónoma de México, P.O. Box, 356, 22800 Ensenada, B.C. México*
Corresponding author: valeri.dzurkov@gmail.com

The detection of ultraviolet (UV) radiation has a wide range of applications, such as environmental, chemical and biological analysis and monitoring. Flame detection, astronomical studies and optical communications are other fields of application of UV detectors. A part of the commercial crystalline Si detectors have been enhanced to detect in the UV range, but they have some drawbacks and therefore most materials used for UV detection are not silicon but compound semiconductors.

In the recent years, silicon oxide containing silicon nanoparticles is considered as a material suitable for UV detection. An important advantage of this material is that its preparation is completely compatible with the contemporary microelectronic technology.

In this study Metal-Oxide-Semiconductor structures with semitransparent Au top electrode and containing Si nanocrystals in the gate dielectric are fabricated and explored. It is shown that the structures can be charged negatively or positively by injecting or extracting electrons from the top electrode. UV illumination with 395-400 nm, 10.4 mW light source causes discharge of previously charged structures with rate which varies between 2 mV/s and 12 mV/s. The discharge rate depends on the sign of the charge trapped in the Si nanocrystals, as well on the internal electric field in the gate dielectric. The effect of UV light on non-charged MOS structures under applied bias has also been studied.

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B.4

Application of Thin Metal Oxide Films in Acoustic Wave Based Chemical Sensors

K. D. Esmeryan

Georgi Nadjakov Institute of Solid State Physics, 72, Tzarigradsko Chaussee Blvd., 1784 Sofia, Bulgaria

Corresponding author: karekin_esmeryan@issp.bas.bg

Acoustic wave (AW) based chemical sensors has attracted considerable interest of the sensor community in the past few decades, because of several features such as high resolution and sensitivity, fast response time, superb overall stability and high dynamic range. The AWs can be classified in three main categories: surface, bulk and guided acoustic waves. In essence, these waves are mechanical vibrations excited in piezoelectric crystals, where the wave velocity of propagation matches the velocity of sound in solids, hence the name acoustic.

The acoustic waves can be generated through interdigital transducers or circular electrodes located on both sides of the piezoelectric crystal. For the case of guided waves an additional metal grating or thin solid film is added to prevent wave diffraction into the bulk. Since AW sensors are fabricated on piezoelectric substrates, the sensing process involves either mechanical or electrical perturbations. Therefore, these devices are sensitive mainly to physical parameters, which may interact with the mechanical and/or electrical component of the wave.

One of the mechanisms used for detection is through an increased mass loading on the sensor surface. This surface is coated with a thin film sensitive to a gas-phase chemical compound of interest. If a certain concentration from the analyte is applied to the sensor surface, gas molecules are absorbed by the sensing layer until the number of absorbed and desorbed molecules becomes equal. During this process, the coating becomes heavier, thus increases the mass loading on the surface. As a result of that, the acoustic wave propagation velocity v decreases and causes a concentration proportional resonance frequency down shift Δf, called sensor signal. Thin metal oxide films are widely used as sensitive layers due to their good sorption properties and adhesion, excellent long-term stability and reproducible sensing characteristics even after hundreds measurement cycles.

Photocatalytic and Gas Sensing Properties of Transition Metal Oxides Nanocomposites Prepared by ALD

***S. Boyadjiev**[1,2], **B. Manduca**[3], **P. Bárdos**[3], **Z. Nagy**[3], **Z. Baji**[4] and **I.M. Szilágyi**[1,3]*

[1]*MTA-BME Technical Analytical Chemistry Research Group, Budapest, Szent Gellért tér 4., H-1111, Hungary*
[2]*Technical University – Sofia, Department of Microelectronics, 8 Kl. Ohridski blvd., Sofia-1000, Bulgaria*
[3]*Budapest University of Technology and Economics, Department of Inorganic and Analytical Chemistry, Budapest, Szent Gellért tér 4., H-1111, Hungary*
[4] *Hungarian Academy of Sciences, Research Centre for Natural Sciences, Institute of Technical Physics and Materials Science, H-1121 Budapest, Konkoly Thege M. út 29-33, Hungary*
Corresponding author: boiajiev@gmail.com

TiO_2, ZnO and WO_3 as n-type semiconductors are widely used photocatalysts and gas sensors. Their properties might be improved by making composites of them with other semiconductor oxides. In the present work, by combining electrospinning, annealing and atomic layer deposition (ALD), pure ZnO, TiO_2, WO_3 and core/shell ZnO/TiO_2, TiO_2/ZnO, and WO_3/TiO_2 nanofibers and nanoparticles were prepared and tested as photocatalysts and gas sensors.

ZnO nanofibers were obtained by electrospinning zinc acetate and polyvinylpyrrolidone (PVP). TiO_2 nanofibers were electrospun from a mixture of titanium isopropoxide ($Ti(iOPr)_4$) and PVP. The as-spun fibers were annealed at 500 °C to remove the polymer part and around 100-500 nm thick and several hundred μm long oxide nanofibers were obtained. Consecutively, ZnO/TiO_2 and TiO_2/ZnO core-shell nanofiber composites were produced by ALD deposition of 4 nm TiO_2 (300 °C using $Ti(iOPr)_4$ and water as precursors) and 4 nm ZnO (200 °C, using diethyl zinc and water as precursors), respectively. WO_3 nanoparticles with controlled structure (monoclinic or hexagonal) and composition (oxidized or partially reduced WO_3) were obtained by annealing hexagonal ammonium tungsten bronze at 500 °C and 600 °C in air or nitrogen. Then core/shell WO_3/TiO_2 nanoparticles were created by depositing 4nm TiO_2 film by ALD.

The formation, composition, structure and morphology of the as-prepared materials were studied by TG/DTA-MS, TEM, SEM-EDX, XRD, UV-VIS, FTIR and Raman spectroscopy. It was investigated how the semiconductor oxides interact with each other when a pure oxide fiber or particle is covered with a thin film of the other oxide, and what is the result of exchanging the core and shell materials. The application of the pure and composite nanofibers and particles was tested in photocatalytic and gas sensing experiments.

Application of Electrochemically Deposited Nanostructured ZnO on Quartz Crystal Microbalance for NO_2 Detection

***B. Georgieva[1]**, M. Petrov[2], K. Lovchinov[2], M. Ganchev[2], V. Georgieva[3] and*
D. Dimova-Malinovska[3]

[1]University of Chemical Technology and Metallurgy, str. Paprat 29, Sofia-1415, Bulgaria
[2]Central Laboratory of Solar Energy and New Energy Sources at Bulgarian Academy of Sciences, blvd. Tsarigradsko chaussee 72, Sofia -1784, Bulgaria
[3]Institute of Solid State Physics, at Bulgarian Academy of Sciences, blvd. Tsarigradsko chaussee 72, Sofia -1784, Bulgaria
Corresponding author: b.georgiewa@abv.bg

The research was fixed on sensing behavior of ZnO nanostructured (NS) films to NO_2 concentrations in the environment.

The ZnO NS layers are deposited by electrochemical method on quartz resonators with Au electrodes. Different time of deposition was applied and the resonators were loaded with three different mass 5.42 µg, 6.68 µg and 16.69 µg, which responded of the quartz crystal microbalance (QCM) frequency shift of 25.05 kHz, 30.29 kHz and 76.24 kHz. The sorption properties of the ZnO thin layers were defined by measuring the resonant frequency shift (Δf) of the QCM-ZnO structure at different NO_2 concentrations. The measurements were based on the correlation between the frequency shift of the QCM and additional mass loading (Δm) on the resonator and Δm was calculated using Sauerbrey equation for the AT-cut quartz plate. In the present work the Frequency –Time Characteristics (FTCs) of all samples were measured as a function of different NO_2 concentrations in aim to define the sorption abilities of the ZnO layers. The experiments were carried out on a special laboratory set up in dynamically regime. From FTCs the response and the recovery times for all kinds of the QCM-ZnO structures were measured varying NO_2. It was obtained, that the sorption of the QCM-ZnO was a function of NO_2 concentration. Frequency shift changed from 23 Hz to 53Hz when NO_2 varying in the range of 250ppm – 5000ppm.

The process of sorption was estimated as reversible and the sorption as physical. The obtained results demonstrated that QCM covered with the electrochemically deposited nanostructured ZnO thin films can be used as application in NO_2 sensors.

B.7

Thin Film Microsensing Elements, Technology and Application in Microsystems for Environment Control

G. Kolev**, **M. Aleksandrova, Y. Vucheva and K. Denishev

Department of Microelectronic of Faculty of Electronic Engineering and Technologies
Technical University of Sofia, blvd. Kliment Ohridski 8, Sofia 1797
Corresponding author: georgi_kolev1@abv.bg

In this paper microsensing elements with thin piezoelectric films are presented. Three different materials from the basic types – ceramic, metal oxide and polymer, in microsystems for environment parameters control are used.

Zinc oxide (ZnO) and Lead Zirconium Titanat (PZT) by sputtering technology from hot pressure targets are deposited. The optimal parameters of the process and thickness of the layers are presented. Layers of piezoelectrical polymer polyviniliden fluoride (PVDF) were prepared by spray deposition technique.

The microelements (MEMS) with these piezoelectric films are proposed for direct and indirect measuring of parameters as pressure, vibration, gas and liquid sensing, fluid flow and etc.

B.8

Influence of the Carbon-based Support on the Electrochemical Behavior of Nanocomposites with Cu-Sn Nanoparticles

***T. Petrov* and I. Markova**

University of Chemical Technology and Metallurgy, 8, Kliment Ohridski Blvd., 1756 Sofia, Bulgaria
Corresponding author: tishenceto@yahoo.com

Cu-Sn nanoparticle powder have been synthesized through a borohydride reduction in a mixture of water solutions of chloride salts and also applying a template technique using a support. As supports for the template synthesis of the Cu-Sn nanoparticle have been used carbon foam (C-foam), carbon powder (C-powder) and graphite.

It has been examined the influence of the support on the formation and phase composition of the obtained nanoparticles. X-ray diffraction (XRD), scanning electron microscopy (SEM), and electrochemical analyses of the carbon-based (C-based) nanocomposites with Cu-Sn nanoparticles have been carried out. Cu_6Sn_5 and $Cu_{10}Sn_3$ phases are formed depending on the support used.

The obtained C-based nanocomposites exhibit a different electrochemical behavior depending on the C-based support and respectively the particle size and their phase composition. According to the carbon matrix different nanocomposites are formed such as graphite/$Cu_{10}Sn_3$, Cu_6Sn_5, Cu_2O; C-powder/Cu_6Sn_5, Cu_2O; C-foam/ $Cu_{10}Sn_3$,Cu,Sn.

The composite of graphite/Cu-Sn alloy is characterized by the highest irreversible discharge capacity of 62%, lower efficiency of the first cycle of 38% and the highest average discharge capacity of 410 mAh g^{-1}, while the composite of C-foam/Cu-Sn alloy is characterized by the highest efficiency at the first cycle of 73%.

POSTERS

Session C

Novel Thin Film Technologies and Applications

Laser Synthesis of Nanometric Iron Oxide Films by Pulsed Laser Deposition

N. Mihailescu*[1], C. Ristoscu[1]*, G. Socol[1], N. Stefan[1], M. Socol[2], S.A. Mulenko[3], N.T. Gorbachuk[4] and I.N. Mihailescu[1]

[1]National Institute for Laser, Plasma and Radiation Physics, PO Box MG-54, RO-77125 Magurele, Ilfov, Romania
[2]National Institute for Materials Physics, PO Box MG-7, RO-77125 Magurele, Ilfov, Romania
[3]Institute for Metal Physics NAS of Ukraine, 36, Academician Vernadsky Blvd., UA-03142, Kiev 142, Ukraine
[4]Kiev State University of Technology and Design, UA-03011, Kiev 11, Ukraine
Corresponding author: carmen.ristoscu@inflpr.ro

We synthesize nanometric thin layers of iron oxide films by reactive pulsed laser deposition with variable thickness, stoichiometry and electrical properties. For deposition, we used an excimer laser KrF* source (248 nm, 25 ns). Substrates of <1 0 0> Si and SiO_2 have been utilized. 4000 to 6000 laser pulses have been applied for the deposition of one film while the ambient reactive oxygen pressure varied from 0.1 to 1.0 Pa.

It was observed that the film thickness depends on oxygen pressure, number of pulses and substrate nature. Films had semiconducting temperature behaviour with variable band gap (E_g) in function of oxygen pressure, substrate nature and temperature. E_g value was in all cases less than 1.0 eV.

We showed by XRD that films deposited on Si substrate were polycrystalline, while films deposited on SiO_2 were amorphous. The higher was oxygen pressure, the lower crystallinity of the deposited film was observed. The effect was a change of thermo electromotive force coefficient (S) value. A better crystallinity was reached for larger substrate temperatures resulting in increased S coefficient value. The largest value of the S coefficient was about 8.7 mV/K for 290–295 K. It decreased to 1.0–1.6 mV/K when heating temperature changed from 240 to 330 K. The figure of merit was ZT = 3–6 in the range 240–330 K with a maximum of 12 at 300–304 K. The use of these nanostructures is suggested for high accuracy thermo-sensing applications.

C.2

ZnO and Hydrophobin Thin Coatings on Textiles Substrates for Biomedical Applications

A.Visan[1], A. C. Popescu[1], G. E. Stan[2], L. Duta[1], G. Dorcioman[1], O. Iordache[3], I. Dumitrescu[3], I. Pasuk[2] and I. N. Mihailescu[1]

[1]National Institute for Lasers, Plasma and Radiation Physics, P.O. BOX MG54, 077125 Magurele, Romania
[2]National Institute of Materials Physics, P.O. Box MG-7, Magurele, 077125, Romania
3National Institute for Textile and Leather, 030508 Bucharest, Romania
Corresponding author: liviu.duta@inflpr.ro

Textile materials can be finished with various functionalization agents in order to ensure new surface properties like antimicrobial, hydrophobicity, resistance to laundering or protection against decoloration.

One well-recognized coating material able to enhance the functionality of cloths is zinc oxide (ZnO).It was shown that ZnO nanopowders have an efficient antibacterial action. Recently, combinations ZnO-organic were tested for various applications requiring antimicrobial properties. Adhesion to substrate and antimicrobial efficiency of pulsed laser-deposited ZnO nanostructures were significantly increased by interposing a buffer nano-layer of hydrophobin.

We suggest a new approach in medical textiles surface functionalization, i.e., to use the intermediate hydrophobin layer beneath a second outer functional oxide layer, in order to augment some of its specific properties. In this respect, we report on the coating with ZnO and hydrophobin adherent thin films of cotton woven fabrics by Pulsed laser deposition technique in order to obtain innovative textile materials, demonstrated protective effects against UV radiations and antifungal action.

The hydrophobin interlayer increased by eight times the ZnO film resilience to wash in water, while in alkaline or acidic artificial sweat, it increased by 2 and 1.2 times, respectively, as compared to textiles covered with ZnO films only. Hydrophobin boosted the biocide effect of ZnO nanostructured films in case of Candida albicans and mold mix inoculum cultures by 50 and 30 %, respectively.

An interpretation of these phenomena is advanced based upon the results of the structural investigations. We studied if the intercalation of a hydrophobin nanolayer between substrate and ZnO film can boost the oxide efficiency against microorganisms with a higher natural resistance, like filamentous fungi. Investigations of the fabricated structures with or without hydrophobin interlayer were conducted and an explanation of observed phenomena was proposed.

Parameter Variation of the One-Diode Model of a-Si and a-Si/µc-Si Solar Cells for Modelling Light-Induced Degradation

***J. A. Weicht*, F. U. Hamelmann and G. Behrens**

University of Applied Sciences Bielefeld, Technical Faculty, Artilleriestraße 9a, 32427 Minden, North Rhine-Westphalia, Germany
Corresponding author: JWeicht@FH-Bielefeld.de

Silicon-based thin film solar cells have a transparent conductive oxide of oxygen-doped zinc or tin oxide as front contact. Amorphous silicon-based (a-Si) solar cells consist of a thin film of a p-i-n structure of amorphous silicon (a-Si). Micromorphous thin film solar cells have a tandem structure of one amorphous and one microcrystalline silicon-based thin film (a-Si/µc-Si): Each has a p-i-n structure. In the presentation of our work we want to show the electrical behavior of a compound of these different kinds of thin film under different climate conditions.

For analyzing the long-term behavior of thin film a-Si/µc-Si photovoltaic modules, it is important to observe the light-induced degradation (LID) in dependence of the temperature for the parameters of the one-diode model for solar cells. According to the IEC 61646 standard, the impact of LID on module parameters of these thin films is determined at a constant temperature of 50°C with an irradiation of 1000 W/m² at open circuit conditions. Until now previous papers examined the LID of thin film a-Si solar cells with different temperatures and some others are about a-Si/µc-Si. In these previous papers not all parameters of the one-diode model are examined. We separate between the serial resistance (R_s), parallel resistance (R_p), short circuit current (I_{sc}), open circuit voltage (U_{oc}), the maximum power point (MPP: Umpp, Impp and Pmpp) and the diode factor (n).

Since the main reason for the LID of silicon-based thin films is the Staebler Wronski effect in the a-Si part of the cell, the temperature dependence of the healing of defects for all parameter of the one-diode model is also taken into account. Also we are measuring to different kind of transparent conductive oxides: For a-Si thin film solar cells we use tin oxide and for thin film solar cells of a-Si/µc-Si we use zinc oxide.

In our work we describe an approach for transferring the parameters of a one-diode model for tandem thin film solar cells into two separated one-diode models for each solar cell.

The measurement of degradation and regeneration at higher temperatures is the necessary base for optimization the different silicon-based thin films in (sub-) tropical regions.

C.4

Electrochemically Deposited ZnO Nanostructured Array on ZnO:V Seeding Layer

***K. Lovchinov*, M. Petrov, D. Dimova-Malinovska**

Central Laboratory of Solar Energy and New Energy Sources at Bulgarian Academy of Sciences, blvd. Tsarigradsko chaussee 72, Sofia -1784, Bulgaria
Corresponding author: sunpoint@solarlab.bg

ZnO nanostructured (NS) array are grown by electrochemical method on conductive seeding layers of ZnO doped with V (ZnO:V) deposited by magnetron sputtering on glass substrates. The surface morphology of the ZnO NS is studied by Scanning Electron Microscopy. The spectra of transmittance, diffused and specular reflectance are measured for the ZnO NS arrays deposited for 30 and 60 min. and are compared to the corresponding spectra of the substrate with seeding ZnO :V film. The values of specular reflectance decrease and those of diffused reflection are higher than those of the seeding layers and increase with the time of electrochemical growth. The deposited nanostructured ZnO array have large effective surface area, demonstrate good antireflecting properties and could be applied in thin film solar cells for increasing light harvesting.

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Biogenic Oxides from Neutrophilic Iron Bacteria and Possibilities for Application in Nanotechnology

R. Angelova[1,2]***, L. Slavov***[2]***, M. Iliev***[1]***, B. Blagoev***[2]***, I. Nedkov***[2] ***and V. Groudeva***[1]

[1] *Faculty of Biology, Sofia University, 8 Dragan Tzankov Blvd., 1164 Sofia, Bulgaria*
[2]*Institute of Electronics, Bulgarian Academy of Sciences, 72 Tzarigradsko chaussee Blvd, 1784 Sofia, Bulgaria*
Corresponding author: angelova87@abv.bg

The neutrophilic iron bacteria are large physiological group bacteria with different taxonomic status but united by their ability to oxidize Fe^{2+} at neutral pH, forming insoluble ferric oxides/(oxy)hydroxides. The oxides formed on their sheaths are of great interest for application in different nanotechnologies and different biomedical and bioengineering applications.

The bacterial mediated formation of iron containing tubular structures, their magnetic properties and behavior are currently poorly understood. It is also not clear why many of the strains do not form sheaths during the cultivation under laboratory conditions.

The goal of this study is to obtain and characterize the ferric oxides/(oxy)hydroxides after cultivation of the bacteria in laboratory conditions. The bio-oxides were obtained by pure cultures of the bacteria isolated from natural habitats and identified by the methods of classical and molecular taxonomy as strains of the genus *Leptothrix*. The characterization of the oxides and sheaths was performed by different physical methods.

Adler medium and Lieske medium were the most appropriate for obtain ferric oxides. Sheaths were formed on SIGP medium. Light micrograph images and SEM unveiled that the average size of the sheaths is about 7 μm, and an average diameter is up to 1 μm. XRD measurements showed the composition of the oxides obtained, as well as the average size of the iron particles (up to 30 nm). TEM micrographs unveiled the shape of the biogenic nanoparticles. The magnetic measurements showed superparamagnetic character of the biomaterials. The composition of the nutrient medium strongly influences the type of the ferric oxides formed.

The analyses revealed a wide range of potential applications of the material obtained as pigments, adsorbents, catalysts, magnetic resonance imaging contrast enhancement, detoxification of biological fluids, drug delivery and in cell separation and others.

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Laser Cleaning – Application for Cultural Heritage Restoration

***V. Atanassova*, S. Karatodorov, G. Yankov, P. Zahariev, K. Dimitrov and M. Grozeva**

Institute of Solid State Physics, Bulgarian Academy of Sciences, 72 Tzarigradsko chaussee,
blvd, 1784 Sofia, Bulgaria
Corresponding author: vatanassova@issp.bas.bg

Laser cleaning is considered as a new alternative processing technique to replace traditional cleaning methods using mechanical and chemical means. It offers many advantages such as selectivity of the interaction with matter, no mechanical contact, highly precise and controlled removal, etc. These characteristics contributed to applying the lasers as reliable tools for Cultural Heritage (CH) restoration.

Different types of lasers sources are used for restoration purposes. For a safe and successful intervention the choice of laser operation parameters, such as laser wavelength, pulse duration, repetition rate, fluence, should be very careful. Some of the most commonly used lasers are Nd:YAG, Er:YAG, CO_2, excimers, etc.

Femtosecond lasers are brand new field of investigation for CH conservation, since the short pulses (ps - fs) were found to overcome many disadvantages of the nanosecond laser pulses, minimizing the photo-thermal, photo-mechanical and photo-chemical phenomena and thus enhancing the laser restoration possibilities.

In this work the application of different types of lasers for CH restoration is reviewed and some case studies are presented.

C.7

Emission Characteristics of the Plasma during Pulsed Laser Deposition of Ferrous Sulfide

S. Karatodorov[1]***, V. Mihailov***[1] ***and T. Křenek***[2]

[1]*Institute of Solid State Physics – Bulgarian Academy of Sciences, bul. Tsarigradsko Chaussee 72, 1784 Sofia, Bulgaria*
[2] *Research Centre of New Technologies, University of West Bohemia, 30614 Plzeň, Czech Republic*
Corresponding author: skarat@issp.bas.bg

Here we report the results of optical emission spectroscopy of the plasma plume during the pulsed laser deposition (PLD) of ferrous sulphide (FeS). The deposition is done with 1064 nm Nd:YAG laser on not-intentionally heated Cu and Al substrates in vacuum.
The plasma plume emission is measured *in-situ* by optical emission spectroscopy with temporal and spatial resolution. The analysis of detected spectra indicates the presence of both Fe and S atomic and ion emission lines.

The temporal and spatial evolution of the intensity of appropriate set of spectral lines are used for the calculation of the plasma parameters. The electron temperature is obtained using the Boltzmann plot method and the electron density is determined using Stark broadening of FeI spectral lines.

C.8

Structural, Optical and Electrical Properties of ZrO_2/Ag/ZrO_2 Multilayer Structure Deposited by R.F. Magnetron Sputtering

K. Lovchinov[1]***, O. Angelov***[1]***, M. Petrov***[1] ***and D. Dimova-Malinovska***[1]

[1]*Central Laboratory of Solar Energy and New Energy Sources, Bulgarian Academy of Sciences,*
72 Tzarigradsko Chaussee, 1784 Sofia, Bulgaria
Corresponding author: lov4@abv.bg

The stacks are deposited on glass substrates by r.f. magnetron sputtering consecutively targets of ZrO_2 and Ag targets. Multilayer structures are studied – deposited at different distances to the target (5.5 cm, 7.5 cm and 10 cm). The properties of the as-deposited and annealed in forming gas atmosphere, at 180^{o}C for 1 h are compared.

The structural properties of the stacks are studied by TEM and SEM images and demonstrate semi-continuous granular structure of the Ag films. The spectra of transmittance and reflectance have bands resulting from interband transitions of d-shell electrons of Ag atoms and plasma resonance oscillations of free electrons.

The resistivity of the as-deposited and annealed stacks is in the range of (1.2 - 1.5) 10^{-5} Ω.cm and practically does not change after annealing.

The deposited stacks have potential for application as a back reflector in thin film solar cells for improvement of light harvesting and their efficiency.

Electron Beam Induced Changes in the Reflectance of Materials

***D. Lyutov**, S. Hadjiiski, K. Kirilov, G. Tsutsumanova, A. Tsonev and S. Russev*

Department of Solid State Physics and Microelectronics, Faculty of Physics, Sofia University
"St. Kliment Ohridski", J. Bouchier 5, Sofia, Bulgaria
Corresponding author: d_lyutov@phys.uni-sofia.bg

Scanning electron microscopy is used for researching of micro- and nanostructures and imaging of the surface of solid materials. In recent years, the scanning electron microscopy is combined with other methods to acquire more information about the properties of the sample. Some new techniques use detection of thermal changes or acoustic signal, induced by the electron beam, to acquire image or to investigate the properties of the sample in local area. These techniques are useful for imaging of ferroelectric domains or inhomogeneities on the surface of the sample.

In our work we combine scanning electron microscopy and ellipsometry to examine the surface properties of the materials. The ellipsometry is very sensitive to changes of optical properties of materials and to changes of the sample's surface. This high sensitivity is only in direction normal to sample's surface while the lateral resolution is much lesser.

The scanning electron microscope has better resolution and the electron beam can induce local changes in the electron density and the temperature of the sample, which alters the reflectance coefficient. This change can be detected by contactless optical methods, in particularly by ellipsometry.

Our purpose is to examine how the reflectance depends on changes of the temperature and the electron density in different polarization state of light.

C.10

Electrochemical Properties of Cell-Mimetic Lipid Membranes Obtained in Cells Consisting of Indium-Tin Oxide Coated Plates and Polymer Spacers

D. Mitkova [1,2]***, R. Dimova***[2] ***and V. Vitkova*** [1]

[1] *Institute of Solid State Physics, Bulgarian Academy of Sciences, 72 Tsarigradsko Shausse*
1784 Sofia, Bulgaria
[2] *Max Planck Institute of Colloids and Interfaces, Science Park Golm 14424 Potsdam, Germany*
Corresponding author: victoria@issp.bas.bg

Scanning electron microscopy is used for researching of micro- and nanostructures and imaging the electrical properties of lipid bilayers are relevant to various cellular functions of neurons, of cardiac or muscle cells. The lamellar structure of cell membranes is determined by their lipid matrix. In the present work we used lipid bilayers as a model system for studying the electrical properties of biological membranes [1]. Palmitoyl-oleoyl phosphatidylcholine (POPC) giant unilamellar vesicles (GUVs) were studied in aqueous solutions of sucrose. GUVs were obtained by electroformation [2] in experimental chambers consisting of indium-tin oxide (ITO) coated plates as electrodes and polymer spacers. In order to prevent the emission of ionic impurities in the aqueous medium ITO electrodes were used in the GUVs' electroformation chambers [3]. Two types of experiments were performed for the measurement of the edge tension and the electrical capacitance of lipid membranes [4,5]. The edge tension of POPC membranes was obtained via electroporation of GUVs by applying strong electrical pulses with short duration 60-80 V/mm for 5 ms and thus, inducing pores in the membrane [6]. Electroporation was applied in symmetric conditions across the lipid bilayer for the concentrations of sucrose from 0 to 400 mM. The capacitance measurements were performed using vesicle electrodeformation under AC fields at frequencies in the range of 0.5-10 kHz [7,8]. The capacitance of POPC bilayers was measured in aqueous solutions of sucrose with several concentrations from 50 to 200 mM with and without 0.1 mM of sodium chloride. The experimental results showed that the membrane capacitance increased with increasing the sucrose concentration in the aqueous medium thus suggesting an effect of the sugar molecules on the studied membrane property.

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_C.11_

Calibration-free Method for Laser-Induced Breakdown Spectroscopy (LIBS)

***I. Neykov* and G. Malcheva**

Institute of Solid State Physics, Bulgarian Academy of Sciences, 72 Tsarigradsko Shoes Blvd.
1784 Sofia, Bulgaria
Corresponding author: ivo@issp.bas.bg

Laser-induced breakdown spectroscopy (LIBS) is an analytical technique of atomic emission spectroscopy that laser-generated plasma is used as the emitting source. In LIBS, a pulsed laser beam is focused by a lens on the target material, of which a small volume is intensely heated and thus brought to a transient plasma state. With high temperature and high electron density, the plasma state, in which the sampled material is broken down, vaporized, atomized, and partially ionized, releases energy by emission of radiation across a broad spectral range between 200 and 980 nm. The atomic and ionic spectra are obtained by means of a spectrograph, thereby allowing elemental components of the target to be identified and quantified.

Commonly, LIBS is used to determine the elemental composition of materials by calibration curves that require several reference samples with the same matrices. This method requires that the measurement conditions of the reference samples match with the measurement conditions of the objects analyzed. Moreover, sometimes making the reference samples that have the absolutely same matrices as the samples analyzed is difficult or even impossible.

Another analytical approach of LIBS for quantifying the elemental composition of materials is the calibration-free LIBS (CF-LIBS). The CF-LIBS determines the concentration of elements by using the mathematic models that describe the plasma emission, not requiring any calibration curves and reference samples. Hence, the CF-LIBS avoids the matrix effect caused by the different matrices between the reference samples and the objects analyzed, and is more suitable to field and on-line applications. The calculation of plasma temperature is a crucial point of the procedure. To increase the reliability of temperature calculation, Saha–Boltzmann method can be used.

C.12

Laser-induced Spectral Analyses

D. Yordanova*, *V. Tankova, G. Malcheva and P. Zahariev

Institute of Solid State Physics, Bulgarian Academy of Sciences, 72 Tsarigradsko Chausee Blvd.
1784 Sofia, Bulgaria
Corresponding author: pezo@issp.bas.bg

The current optical methods for analysis are based on investigating the spectral emission of the plasma, generated at the interaction of a laser beam and the investigated object by laser ablation. The increasing popularity of the laser induced breakdown spectroscopy (LIBS) method is due mainly to the relative simplicity and versatility of the experimental setup for investigating different types of objects – inorganic and organic, solids, fluids, located in various environment: air, gas, liquid. The point of the method is that when focusing a laser beam on a solid surface along with the evaporation of material, plasma is formed, containing atoms and ions with various degree of ionization of the different elements available on the surface. The light emitted from the plasma contains analytical information for the elemental content of the sample. It possesses some special features that make it competitive to the other commonly used methods in archaeology. The characteristics that make LIBS an attractive analytical technique are due to the comparatively simple equipment which is user-friendly, the possibility to reach high spatial resolution, the almost non-invasive and fast implementation of the analysis, the necessity of nearly or no preliminary preparation of the sample that allows the *in situ* analysis. LIBS analysis gives opportunities to investigate solid, liquid and gaseous objects as well as to make quality and semi-quantitative elemental analysis. Moreover, in the implementation of the experiment the single laser pulse and its corresponding spectrum, as well as the results are obtained in several seconds. LIBS technique allows in depth analysis of materials, as the spectra of several successive pulses upon one and the same point of the surface are registered in series.

Laser-induced fluorescence spectroscopy (LIFS) is nondestructive surface analytical technique widely used for identifying the chemical composition of organic and inorganic compounds. It is applied in many fields of human activity due to its simplicity and quickness. LIFS is based on absorption of laser light by material's molecules, being illuminated. Thus excited to upper electronic states, molecules reemit fluorescence light, relaxing to the ground electronic state. The fluorescence spectrum is unique and reproduces its molecular structure. LIFS is versatile, selective and very sensitive technique which could provide spatial and temporal information about an object of any size and material (organic or inorganic) in laboratory or in situ, without the need of sampling or preparation. Lasers offer the advantage of selective excitation within the absorption spectrum of a material enabling high precision in the identification of species. Furthermore, laser sources have the possibility of high-resolution measurements allowing the detection of small quantities of substances or chemical compounds in small area. This method is used in medicine, biology, material analyses and quality control, etc.

LIST OF PARTICIPANTS

Mariya **Aleksandrova** ***I.A.3, B.7***
Technical University Sofia,
Bulgaria
meri_7@abv.bg

Ralitza **Angelova** ***C.5***
Institute of Electronics, BAS,
Bulgaria
angelova87@abv.bg

Iglika **Asenova** ***A.8***
Sofia University, Bulgaria
iasenova@phys.uni-sofia.bg

Victoria **Atanassova** ***C.6***
Institute of Solid State Physics,
BAS, Bulgaria
vatanassova@issp.bas.bg

Georgi **Bodurov** ***A.5***
Central Laboratory of Solar
Energy and New Energy Sources,
BAS, Bulgaria
Joro.bodurov@yahoo.com

Stefan **Boyadjiev** ***B.5***
Technical University Sofia,
Bulgaria
boiajiev@gmail.com

Umut **Cindemir** ***B.2***
Uppsala University,
Sweden
umut.cindemir@angstrom.uu.se

Valeri **Dzhurkov** ***B.3***
Institute of Solid State Physics,
BAS, Bulgaria
valeri.dzhurkov@gmail.com

Karekin Dikran **Esmeryan** ***B.4***
Institute of Solid State Physics,
BAS, Bulgaria
karekin_esmeryan@issp.bas.bg

Kostadinka **Gesheva** ***I.A.2***
Central Laboratory of Solar
Energy and New Energy
Sources, BAS,
Bulgaria
kagesh@phys.bas.bg

Miroslav **Georgiev**
Institute of Solid State Physics,
BAS, Bulgaria
mbarion@abv.bg

Borislava **Georgieva** ***B.6***
University of Chemical
Technology and Metallurgy,
Bulgaria
b.georgiewa@abv.bg

Frank **Hamelmann** ***I.C.8***
Bielefeld University of Applied Sciences
Germany
frank.hamelmann@fh-bielefeld.de

Ekaterina **Iordanova** ***I.C.9***
Institute of Solid State Physics,
BAS, Bulgaria
eiordanova@issp.bas.bg

Victor G. **Ivanov** ***I.D.10***
University of Sofia, Faculty of Physics,
Blvd. James Bourchier 5,
Sofia 1164, Bulgaria
vd_bsc@phys.uni-sofia.bg

Tatyana **Ivanova**
Central Laboratory of Solar
Energy and New Energy Sources,
BAS, Bulgaria
tativan@phys.bas.bg

Yuxia **Ji** ***A.2***
Uppsala University,
Sweden
yuxia.ji@angstrom.uu.se

Radostina **Kamburova**,
Institute of Solid State Physics,
BAS, Bulgaria
radostina.kamburova@gmail.bg

Stefan **Karatodorov** ***C.7***
Institute of Solid State Physics,
BAS, Bulgaria
skarat@issp.bas.bg

Georgi D. **Kolev** ***B.7***
Technical University Sofia,
Bulgaria
georgi_kolev1@abv.bg

Delphine **Lebrun** ***A.6***
Uppsala University,
Sweden
delphine.lebrun@angstrom.uu.se

Konstantin **Lovchinov** ***C.8***
Central Laboratory of Solar Energy
and New Energy Sources,
BAS, Bulgaria
lov4@abv.bg

Dimitur **Lyutov** ***C.9***
Sofia University, Bulgaria
d_lyutov@phys.uni-sofia.bg

Ion N. **Mihailescu** ***I.B.7***
National Institute for Lasers, Plasma,
and Radiation Physics,
Romania
ion.mihailescu@inflpr.ro

Natalia **Mihailescu** ***C.1***
National Institute for Lasers, Plasma,
and Radiation Physics, Romania
natalia.serban@inflpr.ro

Denitsa **Mitkova** ***C.10***
Institute of Solid State Physics,
BAS, Bulgaria
mitkova@issp.bas.bg

Gunnar **Niklasson** ***I.A.1***
Uppsala University,
Sweden
Gunnar.Niklasson@Angstrom.uu.se

Ivo **Neykov** ***C.11***
Institute of Solid State Physics,
BAS, Bulgaria
ivo.neykov@gmail.com

Lars **Österlund** ***I.B.4***
Uppsala University,
Sweden
lars.osterlund@angstrom.uu.se

Miroslav **Petrov** ***C.4***
Central Laboratory of Solar
Energy and New Energy Sources,
BAS, Bulgaria
petrov80@abv.bg

Tihomir **Petrov** ***B.8***
University of Chemical
Technology and Metallurgy,
Bulgaria
tishenceto@yahoo.com

Gianina-Florentina **Popescu-Pelin** ***A.3***
National Institute for Lasers, Plasma,
and Radiation Physics,
Romania
gianina.popescu@inflpr.ro

Georgi **Popkirov** ***I.B.6***
Central Laboratory of Solar
Energy and New Energy
Sources, BAS,
Bulgaria
popkirov@yahoo.com

Bozhidar **Stefanov** ***B.1***
Uppsala University, Sweden
bozhidar.stefanov@angstrom.uu.se

Mihai Adrian **Sopronyi** ***A.7***
National Institute for Lasers, Plasma,
and Radiation Physics,
Romania
mihai.sorponyi@inflpr.ro

Anna **Szekeres** ***I.D.11***
Institute of Solid State Physics,
BAS, Bulgaria
szekeres@issp.bas.bg

Imre Miklós **Szilágyi** ***I.B.5***
Budapest University of Technology
and Economics,
Hungary
imre.szilagyi@mail.bme.hu

Carlos **Triana Estupiñan** ***A.1***
Uppsala University,
Sweden
carlos.triana@angstrom.uu.se

Anita Yoana **Visan** ***C.2***
National Institute for Lasers, Plasma,
and Radiation Physics,
Romania
anita.visan@inflpr.ro

Johannes A. **Weicht** ***C.3***
Bielefeld University of Applied Sciences,
Germany
jweicht@fh-bielefeld.de

Ruitao **Wen** ***A.4***
Uppsala University,
Sweden
ruitao.wen@angstrom.uu.se

Danka **Yordanova** ***C.12***
Institute of Solid State Physics,
BAS, Bulgaria
danka.iordanova@issp.bas.bg