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Contents

Sponsor talks

JEOL TEMs a wide range of cutting edge instruments for each research field

G. Brunetti

JEOL (EUROPE) SAS, 1 Allée de Giverny, 78290 Croissy-sur-Seine, France
E-mail: brunetti@jeol.fr

Since 1949, JEOL's legacy has been one of the most remarkable innovations in the development of instruments used to advance scientific research and technology. JEOL has 60 years of expertise in the field of electron microscopy, more than 50 years in mass spectrometry and NMR spectrometry, and more than 40 years of e-beam lithography leadership.

This presentation is focused on the new JEOL developments of transmission electron microscopes and techniques.

The JEM-2100Plus is a multi purpose transmission electron microscope, which combines the proven JEM-2100 optic system with an advanced control system for enhanced ease of operation. Achieving superior performance through intuitive operation, the JEM-2100Plus provides solutions to a wide range of applications from materials science to medical/biological studies.

For materials sciences and chemistry researches, JEOL proposes the NEOARM (a) with Cold FEG and the new ASCOR Cs corrector represents a radical departure from electron optical technology, achieving unprecedented imaging resolution of 70 picometers with an energy resolution of 0.27eV. ASCOR corrector has been designed to improve the unique performances from 30 to 200kV. The higher brightness and narrower energy spread enabled by the Cold FEG are optimized by the ultra-stable emission, greatly enhancing atom-atom imaging and chemical analysis on a wide high tension range.

The Electrostatic Dose Modulator (EDM) is a fast beam blanking system with a pre-sample electrostatic deflector, including electronics and software control. With EDM, the beam can switch on or off in less than 50 ns. This 100,000x improvement in blanking speed immediately improves the clarity of data taken at fast exposure times. EDM can also attenuate electron illumination without affecting imaging conditions, giving TEM and STEM users exceptional control over the dose on their samples. Cutting-edge electronics and software add-ons unlock advanced applications such as temporal dose structuring and STEM synchronization.

a) 2100Plus

b) NEOARM

c) IDES Products

RGA Mass Spectrometer LEYSPEC – Function and Functionality

Frank Rathmann[1*]

[1]Global Application Management, Scientific Vacuum Division, Atlas Copco
*E-mail: frank.rathmann@vt.atlascopco.com

Keywords: Leyspec, mass spectrometry, residual gas analysis

Quadrupole mass spectrometers are used in many places where conclusions about the composition of a gas mixture are required. For example, such an instrument is ideally suited for monitoring the gas composition required for a process or for detecting contamination. At pressures <1E-4mbar the individual components of the gas are ionised and accelerated towards the so-called mass filter, which only allows particles of a single mass/charge ratio to pass through. The incoming gas particles are detected in the downstream analyser, and the user thus receives information about the proportional composition of the gas mixture. Two different analysers are available. At higher pressure ranges, sufficient measurement can be achieved by using the Faraday Cup, at lower pressure ranges it is recommended to use an additional secondary electron multiplier. The software supplied for operating the device offers the possibility of specific analyses. Depending on your requirements, individual peaks can be displayed as a time curve or you have the option of having the complete gas composition, all full spectrum over the entire measuring range displayed. With the LEYSPEC series Leybold offers 6 instruments which can perform residual gas analyses up to an atomic mass of 100amu for a wide range of applications. The customer can choose between the basic version "View" with measuring ranges up to 200amu or the premium version "Ultra" with measuring ranges up to 300amu. The software included in the scope of delivery enables the device to be parameterised to suit the respective measuring task, but it is also possible to communicate directly with the device by an own control system via the Ethernet interface. In addition, the mass spectrometer has an external display which directly shows the intensity of a freely selectable mass.

Figure 1: Quadrupole mass spectrometer LEYSPEC

Plenary

Plasmonics at the space-time limit

Martin Aeschlimann

Department of Physics and Research Center OPTIMAS, University of Kaiserslautern, Germany
E-mail: ma@physik.uni-kl.de

Keywords: plasmonic nanoantennas, ultrafast nanooptics, plasmon-polariton vortices, orbital angular momentum, time-resolved photoemission electron microscopy (PEEM)

The optical response of metallic nanostructures exhibits fascinating properties: Local field interference effects that lead to strong variations of the near field distribution on a subwavelength scale, and long lasting electronic coherences. To circumvent the experimental limitation of optical diffraction we use a photoemission electron microscope (PEEM) that has been proved to be a versatile tool for the investigation of near field properties of nanostructures with nanometer spatial resolution and subfemtosecond time steps [1,2].

The potential of this technique will be demonstrated on two experiments: In a first work, the long-range energy transfer mechanism between two coupled plasmonic whispering gallery nanoantennas in an elliptical cavity has been investigated. We demonstrate periodic coherent energy transfer back and forth over a distance of twice the excitation wavelength [3]. In a second work we experimentally reveal and measure the spatiotemporal dynamics of the formation of plasmonic vortices and their dressing by optical angular momentum (see Fig. 1). We have manipulated one of the basic properties of light by converting spin angular momentum into orbital angular momentum in a plasmonic Archimedes spiral [4]. By analyzing the time-resolved data in the frequency domain, we show that both single and double angular momentum mixing processes are present, which correspond to different quantum pathways of the electron excitation in 2-photon-photoemission [5].

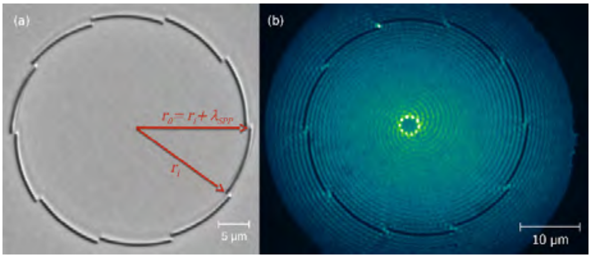

Figure 1. (a) PEEM image of a plasmonic vortex lens of order m=10, imaged using UV light. (b) PEEM image of a structure as in (a), imaged with two circularly polarized laser pulses (hν = 800nm) with a time delay of 55 femtoseconds.

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NIST on a chip: photonic quantum-based measurements for vacuum and beyond

Jay H. Hendricks[*], *Z. Ahmed, D. Barker, K. Douglass, S. Eckel, J. Fedchak, N. Klimov, J. Ricker, J. Scherschligt*[1]

NIST, Physical Measurements Laboratory Sensor Science Division, Gaithersburg MD 20899, USA
E-mail: jay.hendricks@nist.gov

Keywords: Sensors, Standards, Metrology, Photonic, Optical, NIST on a Chip, NOAC, FLOC, CAVS

At the core of the NIST on a Chip (NOAC) program is the idea that measurement technology can be developed to enable metrology to be done "outside the National Metrology Institute" by virtue of deployed and often miniaturized standards and sensors that are based on fundamental properties of nature. More specifically, this plenary lecture will cover NIST efforts in the area of thermodynamic metrology relating to pressure and vacuum measurements. For vacuum measurements, NIST efforts to develop a new a vacuum standard for measuring and understanding the pascal at the lowest pressures through the development of a cold atom vacuum standard will be introduced and discussed. For pressure measurements, NIST efforts to eliminate mercury manometers with a photonic quantum-based measurement that relies on ultra-precise measurements of gas refractive index will be covered.

For vacuum measurements, NIST efforts to develop a new vacuum standard for measuring and understanding the pascal at the lowest pressures are underway. To achieve this, the Cold- Atom Vacuum Standard (CAVS) has been developed which uses a cold atom trap to sense pressure [1]. Since the earliest days of neutral atom trapping, it has been known that the background gas in the vacuum limits the trap lifetime. NIST is inverting this problem to create a quantum-based vacuum standard and sensor. Because the measured loss-rate of ultra- cold atoms from the trap depends on a fundamental atomic property (the loss-rate coefficient, related to the thermalized cross section) such atoms can be used as an absolute sensor and primary vacuum standard. NIST has built a laboratory-scale CAVS apparatus, developed the measurement scheme, and done preliminary theoretical calculations, all of which show promising early results. In addition, NIST is developing a small, portable version that uses a grating-based trap (shown in Figure 1) that will eventually enable users to realize and measure vacuum pressures in their lab without relying on calibrated sensor artifacts [2].

For pressure, the next generation of pressure standards will provide a new route of SI traceability for the pascal [3,4]. In the future, the mercury barometer will be replaced with a new standard based on quantum chemistry calculations. By taking advantage of both the properties of light interacting with a gas and that the pressure dependent refractive index of helium can be precisely predicted from fundamental, first-principles quantum-chemistry calculations, a new route of realizing the pascal has been demonstrated. This technique is very different from classical methods of realizing pressure that have served the metrology community well for the past 375 years. The new photonic-based pressure standards will enable the elimination of mercury manometers, replacing them with a smaller, lighter, faster, and higher precision standard. From a metrology standpoint, the new quantum-based SI pascal will move us from the classical force/area definition, to an energy density (joules per unit volume) definition. Should the technique be further miniaturized, it will lead to a revolution in pressure metrology, enabling a photonics-based device that serves both a gas pressure sensor and a portable gas pressure standard all in one. The new method relies on a pair of optical cavities, each consisting of a set of mirrors on a spacer with the gas/vacuum filling the space between the mirrors. To improve upon this design, the reference cavity is always kept at vacuum to help eliminate noise and other systematic errors. This device, referred to as a Fixed Length Optical Cavity (FLOC), is shown in Figure 2.

The unifying theme is that these efforts are aimed at the development of standards and sensors that are small, deployable, and based on fundamental physics, or are quantum-based. This has been embodied within the "NIST on a Chip" or NOAC program. The key idea of NOAC is that quantum-based measurements are fundamental and when employed in sensors will not require re-calibration. In this embodiment, the standards lab, or in this case "NIST", is "on a chip" and is powerful to industry and society as it means that large networks sensors (or sensors "integrated" into a product or device) can be deployed and trusted to provide accurate measurements without costly re-calibration. A broad summary of the NOAC program will be presented along with the brief overview of the new NOAC Web page [5].

Figure 1. CAVS small portable version NIST prototype with a cloud of trapped Li atoms.

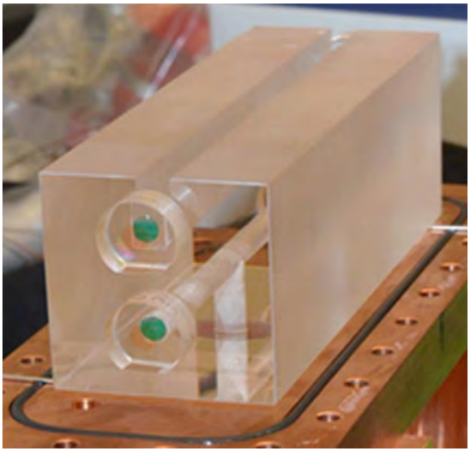

Figure 2. Fixed Length Optical Cavity (FLOC) will replace all mercury Manometers.

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Self-organized nanostructure design in functional nitride alloy films

Lars Hultman

Thin Film Physics Division, Department of Physics (IFM)
Linköping University, Linköping, SWEDEN
E-mail: lars.hultman@liu.se

This presentation reviews strategies for self-organization of nanostructures in functional nitride alloys during physical vapor deposition by virtue of primary and secondary phase transformations. The self-organization is used to enhance mechanical and electronic properties for transition metal and group-III nitride alloy thin films. The structural design is obtained by surface- and bulk-driven phase transformation in metastable TiAlN, ZrAlN, HfAlN, TiSiN, MoVN, VWN, and InAlN model systems, and analyzed by XRD, HREM, FIB, APT, and phase field modeling. *Ab initio* calculations are employed to assess phase stability and decomposition behavior from lattice mismatch and electronic band structure effects. The concept of age hardening in transition metal nitride alloys is reviewed for isostructural model systems. Spinodal decomposition is thus established for TiAlN by the formation of cubic-phase nm-size domains in a checker-board-pattern of TiN and AlN at temperatures corresponding to cutting tool operation. 2-D-nanolabyrinthine structuring in ZrAlN is obtained from with intergrowth of non-isostructural phases *c*-ZrN/*w*-AlN: {110} ‖ {11-20} interfaces. Superhardening in TiN/Si_3N_4 nanocomposites takes place due to Si segregation forming a few-monolayer-thick SiN_x tissue phase, which is a vacancy-stabilized cubic-SiN_x layer. A hardness maximum at 34 GPa – short of ultrahard - is observed in TiN/SiN_x(001) superlattices at the epitaxial-to-amorphous thickness-limit for the SiN_x layers. Thermodynamically-driven Si segregation in c-$Ti_{1-x}Si_xN$ is proven in atom probe tomography on the sub-nm scale using ^{15}N isotopic substitution to resolve mass spectral overlap between Si and N. For $In_xAl_{1-x}N$, we report curved-lattice epitaxial growth of nanospirals with controllable chirality as well as core-shell nanorod formation. Finally, the emerging inherently nanolaminate family of so-called MAX phases is briefly reviewed with examples from Ti_2AlN including for potential non-van-der Waals intercalation.

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Invited Speakers

Superior thermoelectric performance of thin film Heusler alloys

B. Hinterleitner[1,2]*, A. Riss*[1]*, Ch. Eisenmenger*[1]*, T. Mori*[3,4]*, Xing-Qiu Chen*[5]*, E. Bauer*[1,2,*]

[1]Institute of Solid State Physics, Technische Universität Wien, A-1040 Wien, Austria
[2]Christian Doppler Laboratory for Thermoelectricity, Technische Universität Wien, A-1040 Wien, Austria
[3]National Institute for Materials Science (NIMS), International Center for Materials Nanoarchitectonics (WPI-MANA) and Center for Functional Sensor & Actuator (CFSN), Namiki 1-1, Tsukuba, 305-0044, Japan
[4]University of Tsukuba, Tsukuba 305-8671, Japan
[5]Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Science, School of Materials Science and Engineering, University of Science and Technology of China, 110016 Shenyang, Liaoning, China
[*]E-mail: bauer@ifp.tuwien.ac.at

Keywords: thermoelectricity, Heusler compounds, magnetron sputtering

Although full Heusler systems are known for their large power factor, large thermal conductivities allow only moderate ZT values. To overcome such large thermal conductivities, we have prepared Fe_2VAl based alloys as thin films by magnetron sputtering. Subsequent studies on these systems revealed an unprecedentedly large value of the thermoelectric power factor *pf*. Since thermal conductivity is further suppressed for the films in comparison to the bulk material, the figure of merit, *ZT*, is larger than values reported in literature [1]. Various observations have been made, supposed to be responsible for the superior performance of thin films based on Fe_2VAl. Among others, there are i) a meta-stable state which causes a change from fcc to bcc; ii) an electronic density of states exhibiting huge logarithmic energy derivatives, iii) Weyl nodes close to the Fermi energy, and iv) an arrangement of atoms in the crystalline unit cell, reminiscent of high entropy alloys with random disorder on all lattice sites. In this contribution, recent experimental results will be presented and discussed in the context of theoretically derived DFT results.

Acknowledgments

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Recent advances in the field of electron-induced secondary electron emission

Alessandra Bellissimo

Department of Solid State Physics & Microstructure Research, ETH Zürich, 8093 Zürich, Switzerland
E-mail: bellissimo.alessandra@gmail.com

Keywords: Low-Energy Electrons, Secondary Electron Emission, (e,2e)-coincidence spectroscopy, Electron Yield, Field-Emission, Spectro-Microscopy

The impact of an electron beam on a solid surface initiates a cascade of Low-Energy Secondary Electrons (LE-SEs). The energy deposited by the primary electron is distributed and dissipated away over the solid-state electrons throughout a whole manifold of excitation processes, where the first step towards thermalisation always involves the creation and emission of these LE-SEs, independently from the primary energy. Secondary Electron Emission (SEE) is an omnipresent phenomenon, which, in one way or the other, is indisputably crucial to a broad variety of scientific and modern technological applications. On the one hand, their creation can represent a big nuisance, as in the vacuum chambers of charged particle storage rings, where the so-called “electron cloud” formation can lead to a heat load and to a consequent beam-loss during an experiment. A typical problem encountered in UV- and Electron-Beam Lithography is to be ascribed to these LE-SEs, whose random diffusion within the solid limits the attainable lateral resolution in the patterning process. On the other hand, these very same low-energy secondaries are purposely exploited in particle detectors, where the employment of materials exhibiting a high Secondary Electron Yield (SEY) is sought to enhance the collected signal. The few examples mentioned above make clear that to gain control over the phenomenon of SEE is of both fundamental interest and technological significance. This in turn requires a detailed understanding on the elementary mechanisms leading to SEE and although this phenomenon has been investigated since more than a century some of the underlying mechanisms still need to be fully clarified.

This work reports on the recent developments in this field, where the interaction of Low-Energy Electrons (LEEs ≤ 100 eV) with surfaces exhibiting different long-range order was investigated by means of spectroscopic tools of increasing finesse: combining measurements of the Total Electron Yield (TEY) in absolute units, single-electron as well as (e,2e)-coincidence spectroscopy. This investigation has led to an improved understanding on the elementary processes involved in the SE-generation probability, fully taking into account both energy and momentum conservation in the collision, many-body effects – i.e. plasmons – as well as the band structure of the solid [1]. Furthermore, an investigation of the signal generation and contrast mechanism observed in the Scanning Field-Emission Microscope (SFEM) is discussed. Results suggest the formation of a two-dimensional SE-cascade propagating along the surface being responsible for signal generation [2].

Acknowledgments

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Shaping the functionality – 3D micro- and nano-structured thin films for bioelectronics

Vedran Đerek[1], Marta Nikić[1], Katarina Vulić[1], Eric D. Głowacki[2,3,4]*

[1]Department of Physics, Faculty of Science, University of Zagreb, Bijenička c. 32, 10000 Zagreb, Croatia
[2]Laboratory of Organic Electronics, ITN Campus Norrköping, Linköping University, Norrköping, Sweden
[3]Wallenberg Centre for Molecular Medicine (WCMM) Linköping University, Linköping, Sweden
[4]Warsaw University of Technology, Faculty of Chemistry, Warsaw, Poland
[*]E-mail: vdjerek@phy.hr

Keywords: bioelectronics, 3D micro-structuring, organic electronics, field effects

Electrical stimulation of single cells and neurons in a highly localised and wireless manner is an essential milestone towards developing better therapies by stimulation of the autonomous nervous system, for neural prostheses such as artificial retinas, as well as for the use in brain-machine interfaces. A simple and effective device which can survive harsh *in-vivo* conditions and would not harm the living organism during its operation is required for such a task. One example is an organic electrolytic photocapacitor (OEPC), a planar optobioelectronic device based on a *p-n* bilayer of organic semiconductor thin films deposited by vacuum-evaporation of organic pigments. Effectiveness of the OEPCs was demonstrated *in-vitro* by optical electrostimulation of blind retinas [1], on single cells [2], by effecting voltage-gated ion channels of the *Xenopus laevis* oocyte model, and by optical electro-stimulation of peripheral neurons. *In-vivo* stability experiments using laboratory rat model are ongoing, showing stable performance of the devices *in-vivo* over prolonged durations.

We will show how 3D structuring of the OEPCs can simultaneously affect their optoelectronic, bio-electronic and mechanical properties, and thus shape their functionality. Multifold enhancement of the performance of micro-pyramid structured OEPC was measured, and the enhancement depended strongly on the micro-pyramid size and their density. The stimulation light-pulse shaping can further affect the device's bio-electronic functionality by providing transductive electrical potentials of arbitrary shape, duration and polarity to the nearby cells. The paradigm of functionality shaping is thus extended from 3 spatial dimensions to 4D by exploiting the dimension of time.

Acknowledgements

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High rate magnetron sputtering and computer supported modelling as a tool to create complex materials

*C. Eisenmenger-Sittner**, *D. Böhm, J. Kirschner*

Vienna University of Technology, Vienna, Austria
*E-mail: christoph.eisenmenger@ifp.tuwien.ac.at

Keywords: multi element materials, combinatorial sputtering, virtual machine

Magnetron sputtering has achieved major importance not only as a pure deposition technique for the manufacturing of functional coatings, but also as a tool for the design, synthesis and investigation of complex multicomponent materials. The morphological and crystallographic structure of such materials is driven by kinetics and thermodynamics, and often materials are created far from equilibrium, thus exhibiting non-common mechanical, electrical or optical properties. Operating at high deposition rates, as it is possible with high rate magnetron sputtering where deposition rates in the range of microns per minute can be achieved, makes it feasible not only to deposit thin films but also to explore bulk-like materials.

In recent times experimental and computational methods have evolved which not only allow to deposit multi-material systems purely in a co-deposition mode or as a purely periodic layer sequence, but also to couple the real-life deposition system to a computer model of the deposition process. This computer model constitutes a virtual machine which not only acts as a control unit for the deposition plant, but also is capable to predict the coating composition, phase distribution and morphology and to actively interface with the deposition plant to correct deposition parameters when deviations from a planned microstructure are detected. In this talk two cases of a controlled design of multicomponent materials will be discussed. The first case is a systematic study of potential light metal high entropy alloys, where co-deposition in combination with changes in the deposition geometry is employed to produce materials with four and more components with various relative compositions on one substrate. The so obtained systems are thermally treated and then characterized by X-ray diffraction and Scanning Electron Microscopy to identify potential single-phase materials which are stabilized by the high entropy of the system.

Within the second case a Virtual Machine is presented which allows the prediction of the composition, morphology, crystallographic structure and phase composition of a material. Within this system machine readable data on equilibrium phase diagrams, powder diffraction patterns as well as a complete representation of the deposition system are stored. The predictive capability of the Virtual Machine is shown for the simple system Cu-Sn which is deposited at different process parameters, thus exhibiting either a non-equilibrium multilayer structure or its equilibrium phase at elevated temperature.

In conclusion, computer supported multi-material deposition processes will offer a wider range of new possibilities to design specific materials without risking costly and time intensive trial and error experiments.

Acknowledgments

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2D materials heterojunctions with Nitride semiconductors: from synthesis to applications

F. Giannazzo[1,]**, *E. Schilirò*[1], *G. Greco*[1], *G. Nicotra*[1], *F. Roccaforte*[1], *A. Michon*[2], *Y. Cordier*[2], *I. Cora*[3], *A. Koos*[3], *B. Pecz*[3], *R. Yakimova*[4], *A. Kakanakova-Georgieva*[4]

[1]Consiglio Nazionale delle Ricerche, Istituto per la Microelettronica e Microsistemi, Catania, Italy
[2]Université Côte d'Azur, CNRS, CRHEA, Valbonne, France
[3]Centre for Energy Research, Institute of Technical Physics and Materials Science, Budapest, Hungary
[4]Department of Physics, Chemistry and Biology (IFM), Linköping University, Sweden
*E-mail: filippo.giannazzo@imm.cnr.it

Keywords: graphene, MoS_2, Nitride semiconductors, TEM, SPM, high frequency transistors

The integration of 2D materials with group III-Nitride semiconductors (GaN, AlN, InN and their alloys) is currently explored as a platform for novel optoelectronic, ultra-high frequency electronic devices [1] and sensors. In this talk, the fabrication approaches for high quality graphene and MoS_2 junctions with GaN and Al(Ga)N/GaN heterostructures will be discussed. Furthermore, the most recent progresses in realization of ultimately thin 2D layers of GaN, AlN and InN and (see Fig. 1) by the "migration-enhanced encapsulated growth technique" using epitaxial graphene in an MOCVD reactor will be highlighted [2]. Structural, chemical and electrical investigations of these heterostructures with advanced characterization techniques (including atomic resolution TEM and SPM) will be illustrated. Finally, examples of demonstrators based on these material systems will be presented, such as graphene/AlGaN/GaN vertical hot electron transistors for high frequency applications [3] (see Fig. 2), and future developments of these devices will be discussed.

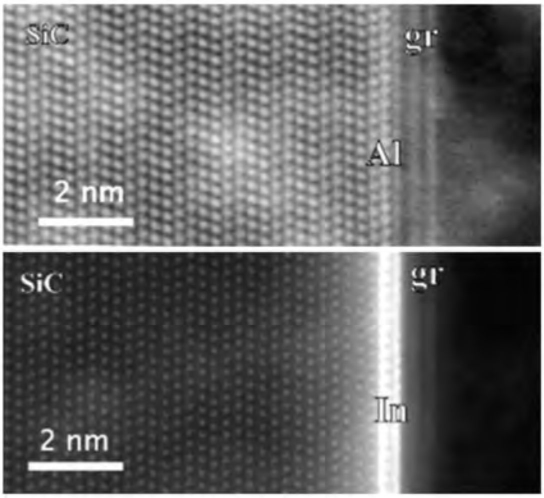

Figure 1: HAADF-STEM images of the graphene/SiC interface intercalated with ultra-thin 2D layers of AlN and InN [2].

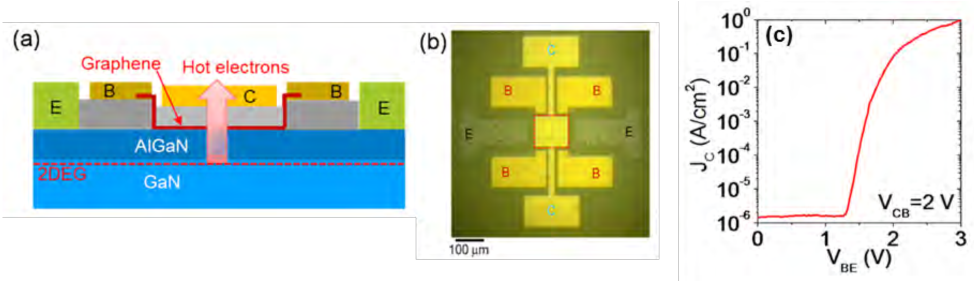

Figure 2: (a) Optical image and (b) transfer characteristic of a graphene/AlGaN/GaN vertical transistor [3].

Acknowledgments

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Single cell biosensing and manipulation on nanostructured optical waveguides

Robert Horvath

Nanobiosensorics Laboratory, ELKH EK MFA 1121 Konkoly Thege M. ut. 29-33, Budapest, Hungary
E-mail: horvathr@mfa.kfki.hu

Keywords: optical biosensor, single cell assay, resonant waveguide grating, micropipette, FluidFM

Label-free methods in life sciences are on the rise. To deeply understand cellular processes at the molecular scale one needs reliable kinetic and structural data, not affected by additional labeling. The Nanobiosensorics Laboratory [1] focuses on the development and application of label-free optical biosensors and combines these technologies with single cell manipulation techniques. Single cell biology is a new research trend, opening up novel directions in cancer research, immunology, and basic biological-biophysical research. This requires the development of powerful technological solution allowing the sensitive monitoring and manipulation of individual living cells, instead of handling large cell populations and measuring population averages.

The short presentation overviews the main features of three planar optical waveguide based techniques routinely employed in our laboratory. Namely, i) Optical Waveguide Lightmode Spectroscopy highlighted to real-time monitor the surface adsorption kinetics, adsorbed footprints and orientation of biomolecules [2], ii) Grating Coupled Interferometry with its outstanding sensitivity to monitor the binding of ions and small molecules to their protein targets [3] and iii) the microplate-based Resonant Waveguide Grating technology, as an excellent tool to characterize cellular adhesion kinetics on model surfaces [4]. Novel ways of combining waveguide sensor technologies with single cell manipulation techniques, such as computer controlled micropipette and robotic Fluidic Force Microscopy (FluidFM BOT), are also discussed. These combinations made possible to calibrate the optical waveguide signals to adhesion force values, and to monitor the adhesion force kinetics of large cell populations for the first time [5].

Acknowledgments

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Plasma-based synthesis of heterogeneous metal/metal and metal/plasma polymer nanoparticles

Ondřej Kylián[1*]*, Jan Hanuš*[1]*, Pavel Solař*[1]*, Radka Štefaníková*[1]*, Anna Kuzminova*[1]*,*
Miroslav Cieslar[2]*, Marek Procházka*[3]*, Hynek Biederman*[2]

[1]Department of Macromolecular Physics, Faculty of Mathematics and Physics, Charles University, Prague, Czech Republic
[2]Department of Physics of Materials, Faculty of Mathematics and Physics, Charles University, Prague, Czech Republic
[3]Institute of Physics, Faculty of Mathematics and Physics, Charles University, Prague, Czech Republic
[*]E-mail: ondrej.kylian@gmail.com

Keywords: gas aggregation sources, nanoparticles, nanomaterials

Low-pressure, plasma-based gas aggregation sources have recently become very attractive tool for the production of various kinds of nanoparticles. The popularity of such sources is given not only by the possibility to produce high purity single material nanoparticles needed for instance in biomedical applications or for ultrasensitive biosensing and biodetection, but also by the fact that they can be easily combined with other vacuum-based deposition techniques that allows for the bottom-up fabrication of complex nanostructured or nanocomposite materials with different architectures and functional properties. Among them highly interesting class of nanomaterials represent two-component heterogeneous nanoparticles. In this study, different strategies suitable for the production of metal/metal and metal/plasma polymer nanoparticles will be reviewed:

i. method based on the use of two-component composite/segmental sputtering targets
ii. multi-magnetron technique, in which two (or more) independently controlled magnetrons are operated in the same aggregation chamber
iii. approach that combines the DC magnetron sputtering with simultaneously running plasma polymerization
iv. strategy that utilizes in-flight coating of single-material nanoparticles produced by a conventional gas aggregation system by an auxiliary plasma source

The advantages/disadvantages of these strategies for the effective and controllable synthesis of nanoparticles with different configurations that range from core@shell or multi-core@shell nanoparticles to nanoparticles that have core-satellite structure will be discussed alongside with their possible applications.

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Combining the gas sensing and resistive switching: thin film semiconductor gas sensors with new functionalities

Tomáš Plecenik, Marek Vidiš, Martin Moško, Samuel Tomašec, Tomáš Roch,*
Leonid Satrapinskyy, Branislav Grančič and Andrej Plecenik

Department of Experimental Physics, Faculty of Mathematics, Physics and Informatics,
Comenius University in Bratislava, 842 48 Bratislava, Slovakia
*E-mail: tomas.plecenik@fmph.uniba.sk

Keywords: gas sensor, resistive switching, metal oxide

The working principle of metal oxide semiconductor gas sensors is based on a resistance change of the gas sensitive oxide layer when exposed to a reducing or oxidizing gas. Recently, a novel type of such sensors with capacitor-like metal/metal oxide/metal electrode arrangement has been proposed [1]. They exploit the high electric field between such capacitor-like electrodes to increase the response (change of resistance) to the target gas. The same or very similar arrangement is also typically used in memristors utilizing the resistive switching (RS) phenomena. In our work, we have merged the two functionalities (gas sensing and RS) in a single capacitor-like Pt/TiO_2/Pt device [2]. It has been demonstrated that the device works well as a gas sensor. However, when it is biased by a constant current, the voltage drop over the device reflects its resistance, which substantially depends on the target gas concentration. If the bias current is chosen appropriately, at certain target gas concentration the voltage exceeds the RS threshold and the resistance state of the device abruptly changes (e.g. from high resistance to low resistance state). A gas concentration change triggered resistive switching is thus observed. The device then rests in the final resistance state, until it is reset by applying high enough voltage of the opposite polarity (in the case bipolar RS). The gas concentration which triggers the RS can be continuously adjusted by the bias current.

We propose that this simple device can be used for long-term monitoring of the environment, since it can (without any additional electronics) permanently store the information about the target gas concentration change above (or below) the set limit. It can also be used as a gas-triggered electrical switch. Thanks to its simplicity, the device can be easily scaled down to a nanometer size and incorporated into other electronic devices.

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Sputter deposited quaternary oxynitrides of transition metals and aluminum

Nina Schalk[1,2*], *Michael Tkadletz*[1], *Christian Mitterer*[1]

[1]Department of Materials Science, Montanuniversität Leoben, Leoben, Austria
[2]Christian Doppler Laboratory of Advanced Coated Cutting Tools at the Department of Materials Science, Montanuniversität Leoben, Leoben, Austria
[*]E-mail: nina.schalk@unileoben.ac.at

Keywords: oxynitrides, sputter deposition, advanced characterization methods, microstructure, mechanical properties

Recently, oxynitrides of transition metals and aluminum have attracted increasing interest due to their tunable properties by adjusting the oxygen/nitrogen ratio. The majority of the existing publications focuses on TiAlON and CrAlON, while only a few reports are available on alternative systems. Considering the enthalpies of formation, it can be assumed that formation of oxides is governed by thermal activation provided during film growth, while for nitrides additional kinetic activation is necessary, indicating that phase formation depends on the involved elements. The differences in the enthalpies of formation also suggest that compositional variations might be present in oxynitrides. However, the verification of such variations is challenging, requiring the complimentary application of advanced characterization methods. In addition, phase formation is also affected by the presence of vacancies, which can be addressed by atomistic modeling within the Density Functional Theory (DFT) framework, capable of providing predictive trends in the formation of possible phases and the influence of vacancies on their stabilization. Thus, the main focus of this presentation is laid on the microstructure and phase composition of different sputter deposited quaternary oxynitride thin films of transition metals and aluminum, garnished with the discussion of their mechanical, electrical and optical properties. Knowledge of the relationship between formation, structure and properties is of vital significance to actively tailor films for different applications.

Innovative coatings for solar radiation management

Andreas Schüler[*]

Solar Energy and Building Physics Laboratory, EPFL, Lausanne, Switzerland
[*]E-mail: andreas.schueler@epfl.ch

Keywords: building-integrated photovoltaics, electrochromic glazing, thermochromic solar selective absorber coatings, semiconductor-to-metal transition

Due to their fascinating optical and electronical properties, nanometer-scaled structures play an important role in solar radiation management. Innovative solar coatings can be made of nanocomposite, nanocrystalline, or nanoporous thin films.

Nanocomposite dielectric films are used in novel multilayered coatings on solar glazing. Such coatings combine a colored reflection with a high solar transmittance and offer new possibilities for the architectural integration of solar collectors in building facades. One widely recognized reference building is the Copenhagen International School, featuring today's largest photovoltaic façade of the world with about 6600 m^2 of active photovoltaic modules.

The use of windows with switchable solar heat gains limits the cooling needs in summer, and decreases the heating needs in winter. The use of inorganic solid-state ion conductors open the pathway to more durable devices, which can be built-up as multilayered film stacks on one glass substrate. The switching speed and contrast, as well as the color neutrality might be considerably improved by novel nanocomposite cathodic and anodic electrochromic layers.

The interesting optical properties of ternary and quaternary spinel-type oxides allow for manifold interband transitions, yielding a dark or even black appearance of many spinel oxides. The remarkable stability at elevated temperatures in air and vacuum makes nanocrystalline spinel oxide coatings an interesting candidate for solar applications involving concentrated solar radiation, such as the generation of solar electricity (concentrated solar power CSP), industrial process heating and solar cooling.

At 68°C, vanadium dioxide undergoes a reversible structural phase transition from monoclinic to tetragonal, accompanied by a semiconductor-metal transition implying strong changes in the electronic and optical properties. The transition temperature can be increased up to 95°C by Ge doping [1], while the hysteresis width and resistivity contrast are gradually decreased. These findings make the use of vanadium dioxide thin films a viable and promising solution for overheating protection of solar thermal collectors. In addition to this, a large variety of novel microelectronics devices has been created, including tunable coplanar waveguide (CPW) bandstop filters, phase-change tunnel field-effect transistor (PC-TFET), and van der Waals MoS_2/VO_2 heterojunctions with tunable rectifying and photosensitive properties.

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Tailoring epitaxial oxide thin film on Si (001) with atomic precision

Matjaž Spreitzer[1*], *Tjaša Parkelj*[1], *Zoran Jovanović*[1,2], *Gertjan Koster*[1,3], *Danilo Suvorov*[1]

[1]Advanced Materials Department, Jožef Stefan Institute, Ljubljana, Slovenia
[2]Laboratory of Physics, Vinca Institute of Nuclear Sciences, University of Belgrade, Belgrade, Serbia
[3]MESA+ Institute for Nanotechnology, University of Twente, Enschede, The Netherlands
[*]E-mail: matjaz.spreitzer@ijs.si

Keywords: Silicon-oxide interfaces, atomic control, $SrTiO_3$, pulsed laser deposition, functional oxides

Epitaxial integration of transition metal oxides with semiconductors offers various phenomena for novel device applications, specifically bringing ferroelectric, ferromagnetic, electro-optic, photocatalytic, multiferroic, piezoelectric and other properties to the well-established silicon platform. A convenient way of integrating functional oxides with Si(001) substrate is through a $SrTiO_3$ (STO) intermediate layer, which can be fabricated on Si(001) in epitaxial form and with high crystallinity using mainly molecular beam epitaxy (MBE) and atomic-layer deposition (ALD) methods. However, slow deposition processes and difficult stoichiometry control make these methods inappropriate from an industrial point of view.

The epitaxial growth of functional oxides on silicon substrates requires atomically defined surfaces, which are most effectively prepared using SrO- or Sr-induced deoxidation and passivation. As-prepared surfaces enable overgrowth with various oxides for novel device applications. In our work pulsed laser deposition (PLD) was used to integrate oxides with silicon. We showed the ability to prepare highly-ordered sub-monolayer SrO- and Sr-based surface structures, including two-domain (2×3)+(3×2) pattern at 1/6 ML Sr coverage as determined by the reflection high-energy electron diffraction (RHEED) technique. On the passivated silicon surface epitaxial layers of STO was grown by the method of kinetically controlled sequential deposition, with out-of-plane relationship of STO(001)‖Si(001) and in-plane relationship of STO[110]‖Si[100]. Detailed study of initial deposition parameters in terms of background gas pressure, deposition temperature, fluence, and oxidation proved to be extremely important in achieving epitaxial relation of STO with the underlying substrate. On as-prepared pseudo-substrate $Pb[Mg_{1/3}Nb_{2/3}]O_3$-$PbTiO_3$ (PMN-PT) films were gown for applications in microelectromechanical systems, due to its high values of longitudinal piezoelectric coefficients and electromechanical coupling. In this presentation growth peculiarities of PMN-PT thin films, including the effect of lead surplus and bottom electrode will also be outlined.

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Atomic-level modification of 2D crystals for catalyzing the hydrogen evolution reaction

Levente Tapasztó

Centre for Energy Research – Institute of Technical Physics and Materials Science, Budapest, Hungary
E-mail: tapaszto.levente@energia.mta.hu

The main appeals of single-atom catalysts are the ultimate efficiency of material utilization and the well-defined nature of the active sites, holding the promise of rational catalyst design. A major challenge is the stable decoration of various supports with a high density of individually dispersed active hetero-atoms. Here we propose that 2D transition metal chalcogenides (TMCs) can provide an efficient template for the stable anchoring of a high-density of individual hetero-atoms through their substitutional incorporation into the TMC crystal lattice. These solid solution TMC catalysts offer the advantages of an easy and versatile synthesis, an unmatched site density, and a stable and well-defined active site structure. The unique features of hetero-atom doped 2D TMC crystals at the origin of their catalytic activity will be discussed through the example of oxygen atoms and platinum clusters incorporated into various TMC single layers.

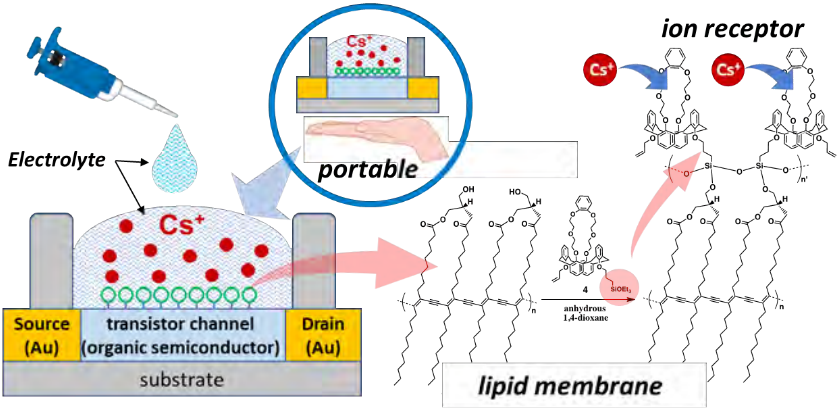
Organic field-effect transistor with lipid membrane for Cs ion sensor

Tin Phan Nguy[1,2], *Ryoma Hayakawa*[1], *Volkan Kilinc*[3], *Matthieu Petit*[3],
Jean-Manuel Raimundo[3], *Anne Charrier*[3], *and Yutaka Wakayama*[1,2*]

[1]International Center for Materials Nanoarchitectonics (WPI-MANA), National Institute for Materials Science (NIMS), Tsukuba, Japan
[2]Department of Chemistry and Biochemistry, Faculty of Engineering, Kyushu University, Tsukuba, Japan
[3]Aix-Marseille University, CNRS, CINaM, Marseille, France
[*]E-mail: WAKAYAMA.Yutaka@nims.go.jp

Keywords: Electrolyte-gated organic field-effect transistor (EG-FET), Cs ion, sensor, lipid membrane

A main purpose of this project is to develop a new ultra-highly sensitive sensor for detecting cesium ions (Cs^+) in natural water. The long-time radioactivity of Cs^+ has serious impact on human health condition. The demand on the detection of such toxic Cs^+ ions has been increased in particular after the catastrophic accident at Fukushima Nuclear Power Station in 2011. In comparison with other conventional methods like ICP-MS and AAS, our new sensor has many advantages: high sensitivity and selectivity, integration and portability, which are associated to real-time monitoring capabilities. The sensor is based on an electrolyte-gated organic field-effect transistor (EG-OFET), which allows high throughput at low cost and portability for frequent on-site measurements. The sensor is consisted of three main components: i) organic semiconducting films with highly stable operation in electrolyte solution, ii) monolayer lipid membrane working as an ultra-thin dielectric layer to allow high sensitivity, and iii) a novel calixarene/crown-ether ion receptor with high selectivity to Cs^+, which is grafted with the lipid membrane[1]. We developed a label-free sensor with the sensitivity of femtomolar (pg/l) concentrations of Cs^+ ion with a high selectivity.



Figures: Right: Schematic illustration of EG-OFET, where electrolyte containing Cs ion is put onto the transistor channel to detect electrical signal from Cs ions. Left: Molecular structure of the calixarene/crown-ether ion receptor grafted on the lipid membrane.

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Liquid Tin: a candidate for liquid metal divertor in future fusion reactors

Rok Zaplotnik[1*], *Vincenc Nemanič*[2], *Janez Kovač*[1], *Miran Mozetič*[1]

[1]Department of Surface Engineering, Jozef Stefan Institute, Ljubljana, Slovenia
[2]Department of Gaseous Electronics, Jozef Stefan Institute, Ljubljana, Slovenia
[*]E-mail: rok.zaplotnik@ijs.si

Keywords: liquid tin, fusion plasma, divertor

Due to the need for reducing greenhouse gas emissions and the increase of energy demands in the future, a new large-scale, sustainable, and carbon-free form of energy is urgently needed. Fusion is worth pursuing because of its advantages: sustainability, no CO_2, no long-lived radioactive waste, limited risk of proliferation, no risk of meltdown, and there is abundant fuel.

There are many fusion reactors around the world, currently the largest being JET (Joint European Torous), where fusion experiments are performed. However, none of these reactors can produce more power than it consumes, the first reactor that will be able to do that is being built in the south of France. ITER tokamak will be a unique experimental tool capable of producing ten times the return of invested energy. However, ITER will not yet be a power plant, but it will contribute to the design of the next-generation machine, a demonstration power plant DEMO.

The divertor, which is positioned at the bottom of the vacuum vessel, controls the exhaust of waste gas and impurities from the reactor and withstands the highest surface heat loads of the tokamak. In ITER, the divertor is made from tungsten, but in DEMO this will not necessarily be the case. The final design of the divertor in DEMO is not yet determined.

For DEMO and beyond, also a liquid metal plasma-facing components are being considered [1]. Only a few metals and alloys with a low melting point have been recognized as suitable candidates, like for example tin, lithium, gallium, LiSn, etc. Currently, tin seems to be the most promising candidate. In order to research the tin properties, experiments are being performed in large scale experiments, such as fusion tokamak COMPAS, and Magnum-PSI [1]. Complementary to those large scale experiments also smaller laboratory experiments are performed in plasma labs such as ours in the Department of surface engineering at Jožef Stefan Institute. Our studies are supported with tasks under EUROfusion work package Liquid Metal Divertor Design (WP DTT1- LMD).

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Zr(–Hf)–Cu based thin-film metallic glasses: properties and thermal behavior

Petr Zeman

Department of Physics and NTIS – European Centre of Excellence, University of West Bohemia,
Univerzitní 8, 306 14 Plzeň, Czech Republic
E-mail: zemanp@kfy.zcu.cz

Keywords: Zr(–Hf)–Cu, thin-film alloys, metallic glasses, magnetron sputtering

Magnetron sputter deposition as a non-equilibrium process with high cooling rates (higher than 106 K/s) is very suitable technique to prepare metallic alloys in an amorphous glassy state as thin-film materials. A short-range atomic ordering of metallic glasses based mainly on icosahedral clusters gives rise to their exceptional physical and functional properties compared to their crystalline counterparts.

Recently, we have successfully prepared binary Zr–Cu [1], ternary Zr–Hf–Cu [2, 3] and quaternary Zr–Hf–Al/Si/Ho–Cu [4] thin-film alloys in a wide composition range by non-reactive magnetron co-sputtering of elemental targets and systematically studied their properties and thermal behavior. All the films were deposited without external heating and bias voltage onto rotating substrates. The films were investigated using several analytical techniques and some experimental results were correlated with and explained by molecular dynamics simulations.

We identified deposition conditions leading to the formation of amorphous Zr(–Hf)–Cu based thin-film metallic alloys with the glass transition, compressive residual stress, enhanced hardness and oxidation resistance, and smooth hydrophobic surface. In case of the Zr–Cu films, a clear correlation between the evolution of the crystallization temperature and mechanical properties with increasing Cu content was observed and explained. In case of the Zr–Hf–Cu films, a gradual substitution of Hf for Zr allowed to tune mechanical properties, the width of the supercooled liquid region and the oxidation resistance. In case of Zr–Hf–Al/Si/Ho–Cu films, an alloying with Al and Si enhanced further mechanical properties, the thermal stability of the glassy state and the oxidation resistance in contrast to an alloying with Ho. Crystallization and oxidation kinetics was studied in detail as well.

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Oral Presentations

T1: Applied Surface Science

Amorphous Ru alloys for durable coatings and ultra-thin free-standing films

*Alessandro Troglia[1], Görsel Yetik[1], Stefan van Vliet[1], Joost Frenken[1,2], Roland Bliem[1,2]**

[1]Advanced Research Center for Nanolithography, Science Park 106, 1098 XG Amsterdam,
The Netherlands
[2]Institute of Physics, University of Amsterdam, Science Park 904, 1098 XH Amsterdam,
The Netherlands
*E-mail: r.bliem@arcnl.nl

Keywords: amorphous alloy, disorder, protective coatings, surface science, photoelectron spectroscopy, nanolithography

Thin-film metallic coatings are a versatile class of materials, finding application for example as protective layers in reducing environments, as low-friction coatings, or as active layers in heterogeneous catalysis. In all but highly specialized applications metallic layers are polycrystalline, consisting of randomly oriented crystallites, separated by grain boundaries. Grain boundaries are known to act as breaking points in the case of strain and as fast diffusion channels for atoms and small molecules [1], compromising desirable properties, such as low permeability, and mechanical and thermal stability.

One simple solution for all these challenges is disorder: Amorphous structure resolves the problems originating in the grain-based nature of thin metal films in the simplest possible way: They do not have grains and, consequently, no grain boundaries [2]. Nature's preference for crystallization, however, makes this solution difficult to achieve for metals and binary alloys. In the present work we report the surprising observation of fully amorphous and thermally stable thin films of a binary Ru alloy, which is not known to form bulk metallic glasses. In their prospective application as protective layers or low-friction coatings such films require all the superior properties that amorphous films provide to withstand reactive environment, radiation, and high temperatures while fulfilling tight constraints on film thickness, roughness, and homogeneity. Using atomic force microscopy, electron microscopy, x-ray diffraction, and photoelectron spectroscopy we characterize the structure and chemical composition of atomically flat amorphous Ru-based layers of various thicknesses up to 200nm deposited onto Si (100) at room temperature. Experiments on their thermal stability show little change in surface composition and morphology up to 400°C; at higher temperatures surface roughening is observed. At 700°C, however, macroscopic flakes of the films delaminate, and the original low surface roughness is recovered. The delamination process results in stable free-standing layers of sizes approaching 1cm^2. Their low roughness, high mechanical stability, and homogeneity are promising characteristics for applications as ultra-thin windows, diffusion barriers, or protective membranes.

In summary, we observe of ultra-smooth, stable, amorphous layers of binary Ru alloys, carrying high potential as protective layers in harsh environments or low-friction coatings. Upon annealing, delamination occurs, yielding free-standing metallic thin films of macroscopic dimensions.

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Effects of gas flooding and temperature manipulation on ionisation efficiency and SIMS depth profiling

Jernej Ekar, Janez Kovač*

Jozef Stefan Institute, Jamova 39, Ljubljana, Slovenia
*E-mail: jernej.ekar@ijs.si

Keywords: secondary ion mass spectrometry, depth profiling, gas flooding, ionisation, matrix effect

Secondary ion mass spectrometry (SIMS), most often combined with time of flight (ToF) analysis, is a type of surface sensitive mass spectrometry method. It works by bombardment of analysed surface with primary ions in a high vacuum ambient. Primary ion impacts cause sputtering of neutral and charged species. The latter are extracted into the analyser where their *m/z* ratio is measured. In this way we gather the information about a chemical composition of analysed surface. With an ion beam of higher current density, one can also perform depth profiling into subsurface region, as in this case, the sputtering is so intense that significant amounts of material are removed. There are number of different primary ions that can be used in SIMS spectrometry. For our research, we used Bi^+ or $Bi_3{}^+$ ions as analytical ion beams and Cs^+ ion beam for surface etching. Our instrument offers dual beam mode approach, which simultaneously applies analytical and etching ion beams. Although in many cases, the depth profiles can be successfully measured in high vacuum (between 10^{-9} and 10^{-8} mbar) at room temperature, there are cases where this approach just isn't sufficient.

To optimise condition appropriate for such situations we performed research focusing on the flooding of analysis chamber with different gases, such as O_2, H_2, CO, up to a pressure of $5 \cdot 10^{-7}$ mbar. We also changed the sample temperature between –150 and 200 °C during SIMS depth profiling. With such modifications we managed to change the sputter rate, ionisation efficiency, sample stability, type of secondary ions emitted and therefore significantly improves SIMS depth profiles. We studied these modifications on different metals and oxides, such as Al, Al_2O_3, Ni, NiO, Cr, Cr_2O_3, Ti, TiN and Si. In our presentation we will discuss the influence of different gases, their pressure and sample temperature on the performance of the SIMS depth profiling. Improved and manipulated ionisation efficiency can also reduce matrix effect, which presents the main obstacle for quantitative SIMS analysis.

Raman study of $(Sc_2O_3)_{0.10}$ $(ZrO_2)_{0.90}$ thin films

Nursultan Kainbayev[1,2*], *Mantas Sriubas*[1], *Kristina Bockute*[1], *Zivile Rutkuniene*[1], *Giedrius Laukaitis*[1]

[1]Kaunas University of Technology, Physics Department, Studentu str. 50, LT-51368, Kaunas, Lithuania
[2]Al-Farabi Kazakh National University, Department of Thermal Physics and Technical Physics, 71 al-Farabi Ave., Almaty, Kazakhstan
[*]E-mail: nursultan.kainbayev@ktu.edu

Keywords: Thin films ceramics, Raman spectroscopy, X-ray diffraction, e-beam physical vapor deposition

Ceramic materials based on Zirconium oxides (ZrO_2) stabilized by rare earth elements as a dopants have a unique set of physical and mechanical properties which could give a big possibility to use in various fields of technology and applications (oxygen gas sensors, oxygen pumps, high-temperature fuel cells) [1, 2]. The crystal structure of pure zirconium at atmospheric pressure in different various of temperature has three polymorphs phases: monoclinic phase (m) is from 25 to 1170 °C, tetragonal phase (t) is from 1170 to about 2370 °C and cubic phase is from about 2370 °C melting point 2680±50 °C. The aim of this work to study the structural phase state of $(Sc_2O_3)_{0.10}$ $(ZrO_2)_{0.90}$ and microstructural analysis of initial powders and thin films [3-4].

In present research Scandia stabilized zirconia ScSZ were deposited with e-beam physical vapor deposition system "Kurt J. Lesker EB-PVD 75", using 0.2 nm/s ÷ 1.6 nm/s deposition rate and temperatures from 50 °C to 600 °C of SiO_2, Alloy 600 (Fe-Ni-Cr), and Al_2O_3 substrates. The initial powders $(Sc_2O_3)_{0.10}$ $(ZrO_2)_{0.90}$ (Nexceris, LLC, Fuelcellmaterials, USA) was used as evaporating material. High-temperature X-ray diffraction (XRD), were used to reveal the phase compositions of initial powders and formed thin films, "Bruker D8 Discover" at 2Θ angle in a 20°–70° range using Cu Kα ($\lambda = 0.154059$ nm) radiation, 0.01° step, and Lynx eye PSD detector. EVA Search – Match software and PDF-2 database were used to identify diffraction peaks. The crystallite size was successfully calculated using Scherrer's equation. Scanning electron microscopy (SEM) "Hitachi S-3400N", were used to investigate the surface of thin films. The ionic conductivity was measured using the impedance spectrometer "NorECsAS" (EIS). The measurements were carried out in 1 ÷ 10^6 Hz frequency range (13 points per decade) and in 200 °C ÷ 1000 °C temperature interval. Raman spectra were recorded at the room temperature, using a Confocal Raman spectrometer Solver Spectrum (NT-MDT). The excitation source was the 532 nm, diameter of laser spot was 2 microns and diffraction grating 1800 providing spectral resolution of $1cm^{-1}$. Laser input power was 20 mW, and 14 mW laser power was in output. Positions of Raman peaks were determined by fitting the data to the Lorentz line shape using a peak fit option in the OriginPro software.

Acknowledgments
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CVD TiC_xN_{1-x} hard coatings: Impact of the C/(C+N) ratio

Christina Kainz[1*], *Christian Saringer*[1], *Michael Tkadletz*[2], *Markus Winkler*[3],
Christoph Czettl[4], *Nina Schalk*[1]

[1]Christian Doppler Laboratory for Advanced Coated Cutting Tools at the Department of Materials Science, Montanuniversität Leoben, Franz-Josef-Straße 18, 8700 Leoben, Austria
[2]Department of Materials Science, Montanuniversität Leoben, Franz-Josef-Straße 18, 8700 Leoben, Austria
[3]Department Thermal Energy Converters, Fraunhofer Institute for Physical Measurement Techniques IPM, Heidenhofstraße 8, 79110 Freiburg, Germany
[4]Ceratizit Austria GmbH, Metallwerk-Plansee-Straße 71, 6600 Reutte, Austria
[*]E-mail: christina.kainz@unileoben.ac.at

Keywords: TiC_xN_{1-x}, hard coatings, fracture, thermal conductivity, oxidation

TiC_xN_{1-x} coatings grown by chemical vapor deposition (CVD), which are commonly used as base layer underneath α-$Al_2O_{3,}$ are subjected to high mechanical and thermal loads during metal cutting. However, the influence of the C/(C+N) ratio on their potential to resist fracture, oxidation and overheating during cutting are not well understood. Thus, within this work, the microstructure, thermo-physical properties as well as oxidation and fracture resistance of CVD TiC_xN_{1-x} coatings were correlated with their composition. Adjusting the C_2H_6/N_2 ratio in the feed gas flow allowed to vary the C/(C+N) ratio freely between 0 and 0.80. All coatings crystallized in a single-phase fcc TiC_xN_{1-x} solid solution. $TiC_{0.47}N_{0.53}$ exhibited the highest hardness (30.0±1.4 GPa), while $TiC_{0.63}N_{0.37}$ turned out as the stiffest coating with a Young's modulus of 576±23 GPa. The fracture stress σ_F and toughness K_{IC} were superior in coatings with moderate C and N content, with $TiC_{0.63}N_{0.37}$ being the strongest ($\sigma_F = 7.7 \pm 0.4$ GPa) and $TiC_{0.47}N_{0.53}$ ($K_{IC} = 4.4 \pm 0.3$ MPa $m^{1/2}$) the toughest within this series. The thermal conductivity decreased with addition of C from 45±5 W/mK in TiN to ~33 W/mK in all ternary TiC_xN_{1-x} coatings. While TiN exhibited a higher oxidation onset temperature (640 °C) than $TiC_{0.63}N_{0.37}$ (550 °C), the ternary coating was only completely oxidized at 850 °C. In conclusion, this work indicates that coatings with a moderate to high C content are more promising for cutting applications than those with low C/(C+N) ratio.

Preferential sputtering and depth resolution in profiling of multilayers with SIMS, XPS and AES

Janez Kovač[1], Siegfried Hofmann[2], Gang Zhou[3], Sandra Drev[1], Jernej Ekar[1], SongYou Lian[3], Bin Lin[3], Yi Liu[3], JiangYong Wang[3]*

[1]Jozef Stefan Institute, Jamova cesta 39, 1000 Ljubljana, Slovenia
[2]Max-Planck-Institute for Intelligent Systems (formerly MPI for Metals Research), Heisenbergstrasse 3, D-70569 Stuttgart, Germany
[3]Department of Physics, Shantou University, 243 Daxue Road, Shantou, 515063 Guangdong, China
[*]E-mail: janez.kovac@ijs.si

Keywords: preferential sputtering, depth profiling, multilayer, MRI model, SIMS, XPS, AES

Thin multilayer film structures are important elements in many fields of advanced technology. Therefore, there is a general demand of for reliable and quantitative characterization of the fabricated layer structures. Among the various methods for this purpose, sputter depth profiling by ion bombardment in combination with secondary ion spectrometry (SIMS), optical emission (GDOES) or electron spectroscopy (XPS, AES) has proved to be versatile and applicable. A convenient means for quantification of depth profiles with an appropriate analysis and reconstruction of a measured depth profile is the Mixing-Roughness-Information depth- (MRI) model [1]. In this presentation a study of multilayer profiles will be given using the MRI model with extension to preferential sputtering [2]. The results show a clear distinction with respect to the main contributions to the depth resolution, namely surface and interface roughness, and atomic mixing. For dominating roughness, the effect of preferential sputtering is more pronounced for the residual surface composition profile (detected by XPS and AES), but it is zero for the sputtered matter composition profile (detected by SIMS). Dominating atomic mixing induced by ion sputtering results in a strong effect of preferential sputtering on the shape of the multilayer profile. This effect is relatively moderate for the XPS or AES depth profiles, but it is surprisingly strong for the SIMS depth profile. Interface width, interface location and layer thickness are always affected by preferential sputtering in XPS and AES depth profiles, but SIMS depth profiles are only affected if the contribution of atomic mixing to depth resolution cannot be ignored. The successful application of MRI model extended for preferential sputtering will be given for fitting an experimental AES depth profile of an Ag/Ni multilayer.

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Room temperature formation of protective nano-coatings by noble gas ion-mixing

A.S. Racz[1], Z. Fogarassy[1], U. Kentsch[3], A. Nemeth[4], P. Panjan[5], Z. Kerner[2], M. Menyhard[1]*

[1]Institute for Technical Physics and Materials Science, Centre for Energy Research,
Konkoly Thege M. út 29-33, H-1121 Budapest, Hungary
[2]Centre for Energy Research, Konkoly Thege M. út 29-33, H-1121 Budapest, Hungary
[3]Institute of Ion Beam Physics and Materials Research, Helmholtz-Zentrum Dresden-Rossendorf,
Bautzner Landstraße 400, D-01314 Dresden, Germany
[4]Wigner Research Centre for Physics, Konkoly Thege M. út 29-33, H-1121 Budapest, Hungary
[5]Jozef Stefan Institute, Jamova 39, Ljubljana, Slovenia
[*]E-mail: racz.adel@energia.mta.hu

Keywords: carbides, ion beam mixing, protective coating

If we irradiate a layer structure at the interfaces atomic mixing, or ion beam mixing (IBM) happens and compound formation, even of high heat of formation carbides, might occur at room temperature. We have shown that this method can be applied to produce protective nano-coatings which are applied in harsh environments [1]. Continuing this trust applying different layer systems nano-layers rich in various carbides meeting application demands are produced by IBM and investigated. C/Si and C/W multilayer structures – with individual thicknesses of 10–20 nm – are irradiated by xenon and argon atoms. The irradiation conditions are chosen with the help of simulation programs (TRIDYN, SRIM). The layer thickness and the in-depth distribution of the formed carbides are investigated by Auger electron spectroscopy depth profiling. We show that the thickness of the carbide-rich region can be tailored by changing the ion irradiation conditions and the layer structure. The corrosion resistance of the layers is tested by potentiodynamic corrosion test. Process-property relationships are discussed.

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Modification of h-BN nanomesh, template for adsorption and catalytic reactions

Ádám Szitás[1], Arnold P. Farkas[2], Krisztián Palotás[2,3], János Kiss[2], Zoltán Kónya[1,2]*

[1]Department of Applied and Environmental Chemistry, University of Szeged, Rerrich Béla square 1, Szeged 6720, Hungary
[2]MTA-SZTE Reaction Kinetics and Surface Chemistry Research Group, University of Szeged, Rerrich Béla square 1, Szeged 6720, Hungary
[3]Institute for Solid State Physics and Optics, Wigner Research Center for Physics, P. O. Box 49, Budapest 1525, Hungary
[*]E-mail: szitas@chem.u-szeged.hu

Keywords: Au nanoclusters, Boron nitride, Rh(111), HREELS

Controlled shape and size distribution of metal nanoparticles for catalytic reactions are important. Through deposition onto the periodic surface of hexagonal boron-nitride (h-BN) [1,2] we can adjust these parameters of gold thereby we are able to influence the catalytic activity of the nanoparticles. In this study we investigated the adsorption properties of ethanol, acetaldehyde and benzene on clean and gold decorated h-BN/Rh(111) surfaces. High-resolution electron energy loss spectroscopy (HREELS) and temperature programmed desorption (TPD) methods have been used on experimental side and density functional theory was applied to model and calculate the possible adsorption energies. In order to map the adsorption properties of the h-BN nanomesh we adsorbed molecules first on the clean h-BN/Rh(111) surface at 140 K. Although, all of the above-mentioned molecules desorbed intact from the clean h-BN monolayer below 300 K, when we adsorbed benzene at 1000 K we developed a graphene-like carbon structure on the BN surface without the removal or destruction of the h-BN film.

On the metal decorated h-BN/Rh(111) system the adsorption properties altered significantly. Ethanol showed enhanced stability on the Au/h-BN/Rh(111) surface [3]. The stabilization effect increases with gold coverage and saturates before Au reaches a continuous adlayer. High selectivity was observed headed for “CO free” hydrogen, a small part of ethanol dissociated to hydrogen and acetaldehyde without further decomposition. Our measurements with acetaldehyde on Au/h-BN/Rh(111) confirmed the expectation that the lack of suitable adsorption sites eliminates the formation of CO. The active sites of gold clusters on h-BN are possibly edge and corner atoms and we need to count with a charge transfer between the substrate and Au which is resulted in negatively charged particles and this way may provide enhanced reactivity of Au/h-BN/Rh(111) [4].

In conclusion, we have examined some industrially important hydrocarbons by sensitive surface science techniques on clean and Au decorated h-BN/Rh(111) systems, keeping in mind the catalytic considerations such as high selectivity.

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Financial supports from the National Research Development and Innovation Office of Hungary projects No. K120115 and No. FK124100 are gratefully acknowledged.

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Secondary electron emission by plasmon induced symmetry breaking in highly oriented pyrolytic graphite (HOPG)

Wolfgang S.M. Werner[1,*], *Philipp Ziegler*[2], *Vytautas Astasauskas*[1], *Alessandra Bellissimo*[2], *Lukas Linhart*[3], *Florian Libisch*[3]

[1]Institut für Angewandte Physik, TU Vienna, Wiedner Hauptstraße 8-10/134, Vienna, Austria
[2]Laboratorium für Festkörperphysik, ETH Zürich, Auguste-Piccard-Hof 1, Zürich, Switzerland
[3]Institut für Theoretische Physik, TU Vienna, Wiedner Hauptstraße 8-10/134, Vienna, Austria
[*]E-mail: werner@iap.tuwien.ac.at

Low energy electrons play an increasingly important role in many modern applications. A prominent example is the secondary electron microscope where SEs are utilized to visualise nanostructured materials. More generally, for the analysis of surfaces low energy electrons are of increasing importance, as exemplified in a most impressive way by recent developments in the field of Low Energy Electron Microscopy (LEEM). In many types of spectroscopy, materials with a high secondary electron yield are employed for detection of charged particles, whereas, in the same instrument, secondary electron emission in the particle optics is usually highly undesired. Low-energy SE may dramatically affect high-energy physics accelerators and storage rings through the multipacting phenomenon. There, formation of an electron cloud may critically affect the heat load to be dissipated away in the cryosystems cooling superconducting magnets. Similarly, the plasma-wall interaction in a fusion reactor is mediated by the electronic emissivity of the reactor walls. SE emission also plays a crucial role in the energy and charge balance of gaseous electronics such as plasma display panels. Charging of surfaces in spacecrafts induced by cosmic radiation can critically affect their operation and lifetime.

Two-particle spectroscopy with correlated electron pairs is used to establish the causal link between the secondary electron spectrum, the $\pi+\sigma$-plasmon peak and the unoccupied band structure of highly oriented pyrolytic graphite [1]. The plasmon spectrum is resolved with respect to the involved interband transitions and clearly exhibits final state effects, in particular due to the energy gap between the interlayer resonances along the GA-direction.

The corresponding final state effects can also be identified in the secondary electron spectrum. Interpretation of the results is performed on the basis of density functional theory and tight binding calculations. Excitation of the plasmon perturbs the symmetry of the system and leads to hybridisation of the interlayer resonances with atom-like s* bands along the GA-direction. These hybrid states have a high density of states as well as sufficient mobility along the graphite c-axis leading to the sharp ~eV resonance in the spectrum of emitted secondary electrons reported throughout the literature.

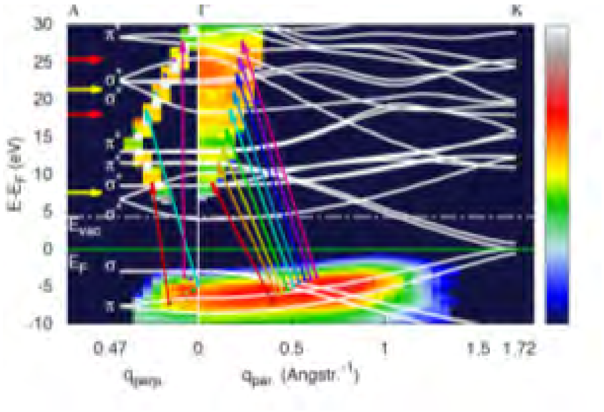

Fig. 1. Measured interband transitions associated with the π+σ-plasmon plotted on the pertinent band structure along the ΓA- and ΓK-direction. The coloured arrows indicate the initial and final states corresponding to the interband transitions associated with the p+s-plasmon.

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T3: Plasma Science & Technique

Effect of positive pulse voltage in bipolar reactive HiPIMS on crystal structure, microstructure and mechanical properties of CrN films

Šárka Batková, Jiří Čapek, Jiří Rezek, Radomír Čerstvý, Petr Zeman*

Department of Physics and NTIS – European Centre of Excellence, University of West Bohemia,
Univerzitní 8, 306 14 Plzeň, Czech Republic
*E-mail: sbatkova@kfy.zcu.cz

Keywords: Bipolar HiPIMS, CrN films, Microstructure, Floating substrate holder, Grounded substrate holder, DC biased substrate holder

High-power impulse magnetron sputtering (HiPIMS) is a deposition method where the high power density in a pulse results in high fraction of ionized species of both the working gas and the target material and broadened ion energy distribution function. This leads to an enhanced ion bombardment of the growing film even without the application of a substrate bias voltage. However, a bias voltage might still be necessary to control the energy of the high amount of low-energy thermalized ions. Lately, bipolar HiPIMS, where the main negative voltage pulse is followed by a positive one, has been suggested to be used instead of a substrate bias voltage, particularly when a DC substrate bias voltage is ineffective.

In this work, we first use a substrate holder at a floating potential to demonstrate that bipolar HiPIMS cannot be used instead of a DC substrate bias voltage for deposition of non-conductive films or deposition onto non-conductive substrates, due to charging and the loss of a plasma-substrate potential difference, necessary for ion acceleration. However, when the substrate holder is grounded, there is an apparent evolution in crystal structure, microstructure and mechanical properties of the CrN films with increasing positive pulse voltage. We compare the effect of the positive pulse voltage in bipolar HiPIMS with the effect of a standard DC bias voltage applied to the substrate holder in unipolar HiPIMS. We find that the effects are different, mainly due to differences in energies delivered into the growing film by bombarding ions. The most interesting properties, namely high hardness (23.5 and 23.1 Pa) at a relatively low residual stress are achieved for films prepared using bipolar HiPIMS with a grounded substrate holder at positive pulse voltages of 90 and 120 V, respectively.

Plasma activation of PMMA thin films: evaluating the polymer cross-linking and degradation with size exclusion chromatography

Tim Egghe[1,2], *Rino Morent*[1], *Richard Hoogenboom*[2*], *Nathalie De Geyter*[1*]

[1]Research Unit Plasma Technology, Ghent University, Sint-Pietersnieuwstraat 41 B4, 9000 Ghent, Belgium
[2]Supramolecular Chemistry Group, Ghent University, Krijgslaan 281 S4, 9000 Ghent, Belgium
[*]E-mail: richard.hoogenboom@ugent.be and nathalie.degeyter@ugent.be

Keywords: plasma activation, PMMA, cross-linking, degradation, size exclusion chromatography

Plasma activation is a versatile and widely used technique for polymer surface modification, in which the resulting surface chemistry can vary largely depending on the employed discharge mixture. Generally, the plasma active species interact with the polymer, leading to different processes like (1) incorporation of new chemical functionalities, (2) polymer cross-linking and (3) polymer chain scission [1]. Direct measurement techniques like X-ray photoelectron spectroscopy (XPS) have elaborately proven the incorporation of new chemical functionalities during plasma activation. In contrast, the second and third processes are investigated to a much lower extent [1-3]. Therefore, this study aims at investigating the relative importance of polymer degradation and cross-linking upon standard plasma treatment conditions by measuring the molecular weight distribution of a model polymer, polymethylmethacrylate (PMMA), via a multi-step analysis process based on size-exclusion chromatography (SEC). First, thin films of PMMA were deposited on glass substrates via spin coating. Then, multiple samples were exposed to a plasma activation step, after which they were incubated in chloroform to dissolve the plasma treated PMMA. The resulting polymer was obtained by evaporating the chloroform, followed by re-dissolving it in *N,N*-dimethylacetamide for the SEC measurement. The plasma activation was performed with a dielectric barrier discharge in different discharge gases (Ar, He, N_2) operating at 5 kPa. The treatment time was optimized by determining the saturation point in the wettability with water contact angle measurements. All SEC measurements indicated that degradation of the polymer chain is the main process and only the Ar-treated sample showed cross-linked polymer chains. From these results, it can be concluded that this research further establishes a method for the evaluation of the polymer degradation and cross-linking upon plasma activation, which could be applied to compare this phenomenon in different plasma reactors.

Acknowledgments

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Molecular dynamics simulation of Si and SiO_2 etching by silicon halide ions

A.Y Jaber [*], *Michiro Isobe, Satoshi Hamaguchi*

Center for Atomic and Molecular Technologies, Osaka University
2-1 Yamadaoka, Suita, Osaka 565-0871, Japan
[*]E-mail: jaber@ppl.eng.osaka-u.ac.jp

Semiconductor devices are the core of information and communication technologies. Semiconductor devices are made of various materials, including silicon (Si), silicon dioxide (SiO_2) or silicon nitride (SiN). In plasma etching processes that are used to form complex device structures on the surfaces of such materials, etched materials enter the plasma and may return to the surface as incident ions. For example, in an etching of a Si surface by a chlorine-based plasma, Si atoms removed from the surface may enter the plasma and form silicon chloride molecules and radicals in the gas phase. Some of such gas-phase species may return to the surface as energetic silicon chloride ions $SiCl_x^+$ with $x = 0 \sim 4$. The goal of this study is to evaluate the sputtering yields and other etching properties of Si and SiO_2 surfaces by incident silicon chloride and silicon fluoride ions as functions of the ion kinetic energy, using molecular dynamics (MD) simulation [1]. The sputtering yields obtained from the simulations were also compared with those obtained from ion beam experiments [2] and they were found to be in reasonable agreement in most cases. The results have also shown that, while the Si atoms of incident silicon halide ions tend to deposit, the halide atoms tend to etch the Si or SiO2 surface, so that the sputtering yield is determined by the balance of these two opposite tendencies. The depths of halide mixed layers formed on the etched surfaces and the distributions of etched species at various incident ion energies were also evaluated by MD simulations.

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Molecular dynamics simulations of nano-scale trench etching of Si by chlorine plasmas

Nicolas Mauchamp[1], Michiro Isobe[1], Jun-Chieh Wang[2], Jason Kenney[2], Shahid Rauf[2], Satoshi Hamaguchi[1]*

[1]Center for Atomic and Molecular Technologies, Osaka University 2-1 Yamadaoka, Suita,
Osaka 562-0871 Japan
[2]Applied Materials, Inc. 1140 E Arques Ave., Sunnyvale, CA 94085 United States
[*]E-mail: mauchamp@ppl.eng.osaka-u.ac.jp

Keywords: MD simulations, nano-scale etching

Plasma etching is a key technology for the manufacturing of semiconductor devices. Micro- and nano-scale structures of materials such as silicon (Si) and silicon dioxide (SiO_2) can be formed by plasma etching. As typical sizes of such devices are approaching the atomic scale, the manufacturing processes are becoming more challenging and require a deeper understanding of the etching mechanisms to achieve better control of etched profiles, surface roughness, material selectivity, and induced damage. Halogen-based plasmas are widely used for etching of Si as they provide high etching selectivity of Si over SiO_2. In this work, molecular dynamics (MD) simulations are used to study reactive ion etching (RIE) processes of nano-scale Si structures by chlorine (Cl) ions and radicals. The goal is to understand the time evolution of the etched profiles, surface roughness, and the surface chemical composition during the etching process in a self-consistent manner.

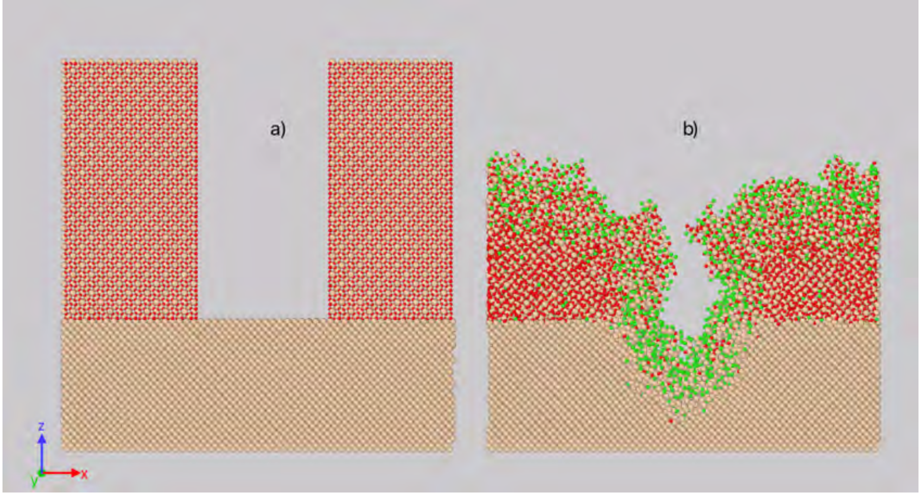

Figure 1: a) Initial substrate. b) Substrate after the 100 eV Cl ion injection with a dose of 2.79×10^{16} cm^{-2}.

The model system studied in this work is composed of a crystalline Si substrate, on which a thin crystalline SiO_2 mask is placed with a few nanometers wide opening (Fig 1a). The typical mask thickness and opening width are 10 nm and 5 nm, respectively. The system is exposed to energetic Cl^+ ions at a normal angle of incidence, possibly with thermal Cl radicals. In typical etching conditions, we expect a 5 nm wide trench of Si to form after the structure is exposed to a Cl plasma (ions and radicals) for an extended period of time. In the atomic scale, however, modified surface layers (i.e., surface layers containing Cl atoms) formed by incident Cl ions and radicals can be comparable in size with the structures to be etched, which causes some phenomena specific to the atomic scale. For example, although the etching rate of SiO_2 is much lower than that of Si under Cl plasma exposure, the SiO_2 mask initially becomes Si rich by preferential sputtering of oxygen (O) atoms. On the other hand, the crystalline Si exposed to Cl ions and radicals initially swells, and its height increases as it amorphizes and incorporates incident Cl atoms. In addition, the mechanical strength of the modified surface layer seems to have significant effect on atomic-scale topography modification. For example, the SiO_2 mask can easily collapse if its oxygen content is depleted sufficiently during the etching process. If the ion energy is kept sufficiently low and the mask does not collapse, etching of Si takes place with a visible redeposition of Si and O atoms on the sidewalls of the trench after a sufficient ion dose (Fig 1b). The formation of volatile desorbed species such as $SiCl_4$ is essential to avoid excessive redeposition on the side walls.

Reduced TiO_2 nanoflake structures with enhanced photoelectrochemical performance by Ar/H_2 DC plasma

Elham Khorashadizade[1,2], Shiva Mohajernia[1], Seyedsina Hejazi[1], Naimeh Naseri[2], Omran Moradlou[3], Alireza Z. Moshfegh[2,4], Patrik Schmuki[1,5*]*

[1]Department of Materials Science, WWIV-LKO, University of Erlangen-Nuremberg, Erlangen, Germany
[2]Department of Physics, Sharif University of Technology, Azadi Avenue, Tehran, Iran
[3]Department of Chemistry, Alzahra University, Vanak Village Street, Tehran, Iran
[4]Institute for Nanoscience and Nanotechnology (INST), Sharif University of Technology, Azadi Ave., Tehran, Iran
[5]Department of Chemistry, King Abdulaziz University, Jeddah, Saudi Arabia
[*]E-mail: moshfegh@sharif.edu, schmuki@ww.uni-erlangen.de

Keywords: reduced TiO_2, hydrothermal method, water splitting, Ar/H_2 DC plasma

Energy supply demand is the most critical concern in recent years. TiO_2 due to its chemical stability, low cost and suitable band position for H_2 and O_2 generation from water, is a promising material for application in photoelechtrochemical fuel production [1,2]. In the present work, thin layers of titanium dioxide with nanoflake morphology (TNFs) are fabricated on Ti foil by simple hydrothermal method. Then, obtained nanostructures are reduced by Ar/H_2 (90/10) DC plasma with UHV chamber at room temperature. The effect of plasma power (5W, 15W and 45W, named R-TNFs-5W, R-TNFs-15W and R-TNFs-45W respectively) is investigated on photoactivity and photoelctrochemical performance of the photoanodes.

The incident photon to electron conversion efficiency (IPCE) results of non-reduced TiO_2 and reduced samples (TiO_{2-x}) at 500 mV vs. Ag/AgCl in a 0.1M Na_2SO_4 solution show a significant enhancement for the TiO_{2-x} photoanodes compare to the non-reduced structure in the UV region. The photoanode reduced at 5W Ar/H_2 plasma has the highest IPCE value of around 20% which is four times higher than IPCE value of non-reduced sample (5%). The improvement in photoelectrochemical performance can be ascribed to the enhancement in conductivity which is caused by introducing Ti^{3+}/ oxygen vacancy states in the reduced nanostructures.

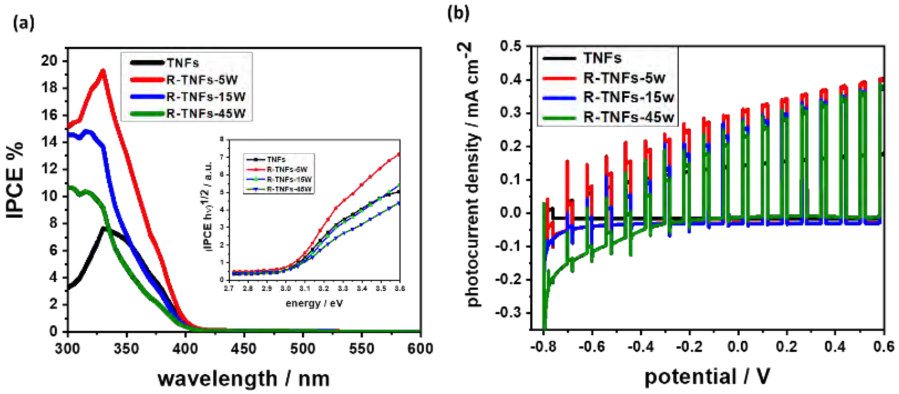

Fig. 1. (a) IPCE values and (b) water splitting efficiencies of black TiO_{2-x} photoelectrodes treated in Ar/H_2 plasma with 5, 15, and 45 W power of system.

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Molecular dynamics simulations of silicon nitride atomic layer etching by hydrofluorocarbon plasmas

Jomar Tercero[1,2*], *Michiro Isobe*[2], *Magdaleno Vasquez, Jr.*[1], *Satoshi Hamaguchi*[2]

[1]Department of Mining, Metallurgical, and Materials Engineering, University of the Philippines, Diliman, Quezon City, 1101, Philippines
[2]Center for Atomic and Molecular Technologies, Osaka University, 2-1 Yamadaoka Suita, Osaka 565-0871, Japan
[*]E-mail: jutercero@ppl.eng.osaka-u.ac.jp

Keywords: molecular dynamics simulations, atomic layer etching, silicon nitride

Controlled atomic-scale etching of semiconductor devices has been studied for decades, following the technology device roadmap of the electronics industry [1-3]. Experimental results have shown that, in atomic-scale device fabrication of nanostructured systems, atomic layer etching (ALE) of silicon nitride (Si_3N_4) typically leads to an etch stop. To investigate this phenomenon, molecular dynamics simulations of a plasma-assisted ALE, which consists of two alternating steps, have been employed (Fig. 1). The adsorption step, where chemically reactive species such as hydrogen-rich (CH_2F) and fluorine-rich (CHF_2) hydrofluorocarbon radicals, was introduced in the system to chemically modify the Si_3N_4 surface. Then the desorption step, where the system is exposed to energetic Ar^+ ions, was employed to sputter off surface atoms. The effects of H and F concentrations in the adsorbed layer as well as Ar^+ ion injection energy on the Si_3N_4 ALE were investigated. Initial analysis of the results has shown that excessive carbon accumulation resulting from the formation of the silicon carbide (SiC) layer causes the etch stop. At low Ar^+ ion injection energy, surface atoms are expected to be removed via the formation of volatile compounds caused by surface chemical reactions. On the other hand, physical sputtering is expected to dominate the removal process of surface atoms at high Ar^+ ion injection energy.

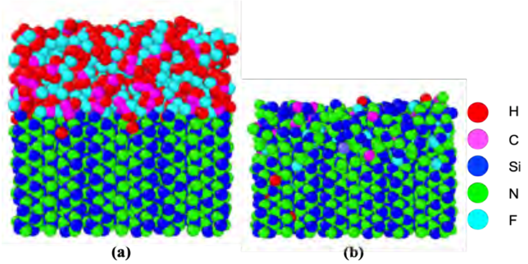

Figure 1 (a) Si_3N_4 with a 2 nm HFC layer in the adsorption step and (b) the removal of the adsorption layer after 100 eV Ar^+ injection with an ion dose of 5.32×10^{16} cm^{-2}.

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Molecular dynamics study on damage formation in atomic layer etching of Si with halogen radicals

Erin Joy Capdos Tinacba[*]*, Michiro Isobe, Satoshi Hamaguchi*

Center for Atomic and Molecular Technologies, Osaka University, 2-1 Yamadaoka, Suita,
Osaka 565-0871, Japan
[*]E-mail: erintinacba@ppl.eng.osaka-u.ac.jp

Keywords: ALE, molecular dynamics simulation, plasma etching

Atomic layer etching (ALE) has gained much attention in the past years as an essential technique in fabrication processes of nano-scale semiconductor devices. ALE is a technique to achieve an atomic-scale control of an etching process by separating it into two steps; adsorption and desorption. In the adsorption step, the surface is modified by depositing a monolayer or thin layer of less reactive molecules. In plasma enhanced ALE (PEALE), the modified layer is removed in the desorption step with the bombardment of energetic ions such as Ar^+. Ideally these ions should not be energetic enough to continuously etch an unmodified or a clean surface. This is called a self-limiting process of ALE. However, more often than not, non-ideal ALE, i.e., ALE without a complete self-limiting process, is utilized in semiconductor fabrication. In non-ideal ALE, more than one monolayer is removed and the sub-layer of the material may be damaged by excessive ion bombardment. Such damages can be critical on some electronic properties of the materials.

In this work, molecular dynamics (MD) simulation [1] was employed to have a deeper understanding of the reaction mechanisms and damage formation during ALE of Si with F, Cl, or Br adsorption and low-energy Ar^+ ion bombardment. The Ar^+ ion energy was varied from 20 to 60 eV. Six cycles of adsorption and desorption steps were simulated and the results were compared with experimental observations [2-4]. It was found that the etch-per-cycle (EPC) value was typically lower during the first cycle compared to the succeeding cycles because the first cycle was mostly spent for the formation of a modified layer. After the first cycle, a reproducible EPC value was observed. The effects of Ar^+ ion bombardment on the modified surface as well as its Si sub-layer were also investigated. It was observed that, even at low Ar^+ ion incident energy (20 – 30 eV), the Si sub-layer is damaged in the desorption step and the extent of this damage increases with increasing energy.

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Pi-Radical as potential candidate for Radio Frequency Scanning Tunneling Microscopy study

Radovan Vranik[1], Vitalii Stetsovych[1], Simon Feigl[1], Stefan Müllegger[1,2]*

[1]Department of Solid State Physics, Johannes Kepler University, 4040 Linz, Austria
[2]Linz Institute of Technology, Johannes Kepler University, 4040 Linz, Austria
[*]E-mail: stefan.muellegger@jku.at

Keywords: RF-STS, resonance phenomena, stable radical

Stable organic radicals serve as model systems for investigating metal-free magnetic phenomena at (sub)nanometer length scales. I will present a single-molecule study of the archetypal stable pi-radical 2,2-diphenyl-1-picrylhydrazyl (DPPH) physisorbed on Au(111) which was done by low-temperature scanning tunneling microscopy (STM) and -spectroscopy (STS) under ultrahigh vacuum conditions. The revealed structural details of the adsorption configuration as well as the frontier orbital-related electronic structure provide a basis for further studies by radio frequency STS (RF-STS) method, a novel technique developed to investigate resonance phenomena at single-molecular level. Such phenomena include excitation of mechanical degrees of freedom of single molecules or molecular clusters as well as nuclear and electronic spin transitions. The latter case was already achieved on a different model system. In case of the DPPH radical a Kondo-like spectroscopic signature was observed within the presented study, indicating the preservation of the unpaired electron spin state of the DPPH monomer on Au(111). This makes it a potential candidate for RF-STS experiments.

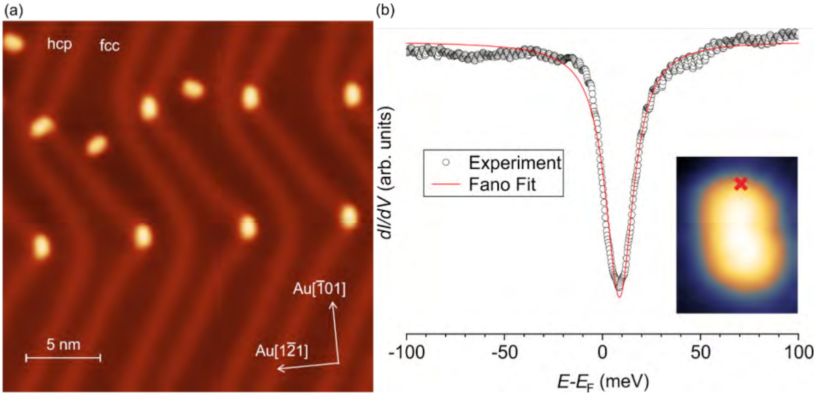

Figure 1. DPPH radical on Au(111):
a) STM topography;
b) dI/dV spectrum with Kondo-like signature.

Acknowledgments

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T4: Surface Engineering

Investigation of structure and properties of doped amorphous carbon films deposited by magnetron sputtering

Vilius Dovydaitis[1*]*, Liutauras Marcinauskas*[1]*, Paola Ayala*[2]*, Aleksandras Iljinas*[1]*,*
Juan Carlos Moreno[2]*, Johnny Chimborazo*[2]*, Claudia Berkmann*[2]

[1]Department of Physics, Kaunas University of Technology, Studentų 50, LT-51368 Kaunas, Lithuania
[2]Faculty of Physics, University of Vienna, Strudlhofgasse 4, 1090 Wien, Austria
[*]E-mail: vilius.dovydaitis@ktu.edu

Keywords: doped, amorphous carbon, Raman, hardness, magnetron sputtering

Metal and oxygen containing amorphous carbon films were deposited using layer by layer magnetron sputtering technique. Coatings were formed by sputtering graphite and metal (Cr, Ti, Ni) targets in low vacuum argon environment. The influence of metal content and type on the doped carbon films surface roughness, structure, microhardness values, wettability and optical properties were determined. The optical measurements indicated that films were highly transparent in near infrared range, however only Cr and Ti doped carbon films were transparent in visible light range. The influence of metal-oxygen doping on the structure of carbons films were investigated using multiple (458 nm, 488 nm, 514 nm and 633 nm) wavelength excitation Raman spectroscopy. Dispersive behaviour of D and G peaks and I_D/I_G ratio changes showed that the increase of metal content resulted in enhanced sp^2 sites fraction.

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Randomly oriented nanowires as sensors for surface-enhanced Raman spectroscopy

Hrvoje Gebavi[1,2*], *Vlatko Gašparić*[1,2], *Nikola Baran*[1,2], *Mile Ivanda*[1,2]

[1]Ruđer Bošković Institute, Division of Materials Physics, Laboratory for Molecular Physics and
Synthesis of New Materials, Bijenička cesta 54, Zagreb, Croatia
[2]Center of Excellence for Advanced Materials and Sensing Devices,
Research Unit New Functional Materials, Bijenička cesta 54, Zagreb, Croatia
*E-mail: gebavi@yahoo.com

Keywords: flexible hot spots, horizontal silicon nanowires, 4-mercaptophenylboronic acid, surface-enhanced Raman spectroscopy (SERS), vapour–liquid–solid

Nanostructured materials plated with metallic layer is a unique category within material science which explores numerous phenomena such as localized surface plasmon resonance (LSPR). Free metal electrons oscillations resonating with the visible excitation photons give strongly enhanced electric field in the nanostructure vicinity. This phenomenon is strongly utilized for ultrasensitive, fingerprint selective, fast analysis and an economical technique known as SERS i.e. surface-enhanced Raman spectroscopy.

This paper is predominantly focused on fabrication and optimisation of the SERS substrates consisting of randomly oriented nanowires. The fabrication methodology includes fabrication of Si or ZnO nanowires on a wafer or optical fibre substrates utilizing 'Vapour-liquid-solid (VLS)' method within 'low-pressure chemical vapour deposition (LPCVD)' reactor or 'Chemical vapour deposition (CVD)'. SERS substrates’ optimization includes nanostructuring, and Ag metal plating by sputtering. The particularity of these specific silicon nanowires (SiNWs) is in their flexibility i.e. a possibility to shrink in bundles upon liquid immersion offering additional SERS signal enhancement. The morphological characteristics and the influence of sputtering are described by the fractal dimension and lacunar analysis.

Finally, SERS substrates were characterized utilizing 4-mercaptophenylboronic acid (4-MPBA) as the test molecule. The laboratory substrates compared with the commercially available substrates showed excellent characteristics.

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2D nanoparticle density gradients: theoretical and experimental study

J. Kratochvil[1], J. Kousal[2], P. Kus[2,3], P. Sezemsky[1], O. Kylian[2], V. Stranak[1]*

[1]Institute of Physics, University of South Bohemia in Ceske Budejovice, Czech Republic
[2]Department of Macromolecular Physics, Charles University, Prague, Czech Republic
[3]Department of Surface and Plasma Physics, Charles University, Prague, Czech Republic
[*]E-mail: kratji@seznam.cz

Keywords: 2D, gradient, nanoparticle, nanostructure, bio

Thin films with laterally graded physicochemical properties finds utilization in many applications as combinatorial substrates [1], e.g. for tissue engineering, tailored wettability etc. Furthermore, graded films formed by plasmonic nanoparticles (NPs) dispose with high added value as an active substrates for e.g. biomolecules detection by surface enhanced Raman spectroscopy (SERS).

We will present the theoretical as well as experimental study of highly defined 2D-graded two-metal nanocomposite surfaces that are nearly impossible to prepare by wet chemistry. The 2D graded NPs based nanostructures were prepared by utilization of nanoparticle beam produced by gas aggregation source of nanoparticles. We introduce analytical model which enables to describe and design planar surface (x, y) with 2D graded properties, e.g. with linear, exponential, or logarithmical distributions of NPs. The theoretical description of 2D gradients is based on two surface functions (i) nanoparticle volume surface density V_{NPs} and (ii) volume chemical composition ratio Ω_A. Practically each substrate point (x, y) can serve as the separate unique sample with different surface density and chemistry.

The theoretical description was proved experimentally by deposition of 2D-linear Ag-Cu nanoparticle gradient, which represents the gradient with simplest analytical description by V_{NPs} and Ω_{Ag} functions as is shown in Figure. Therefore, such NPs gradient represent substrate with high application potential which we will demonstrate on surface with 2D graded double-peak localized surface plasmon resonance. We show that amount of NPs and chemical composition ratio varies more or less linearly along the substrate diagonals.

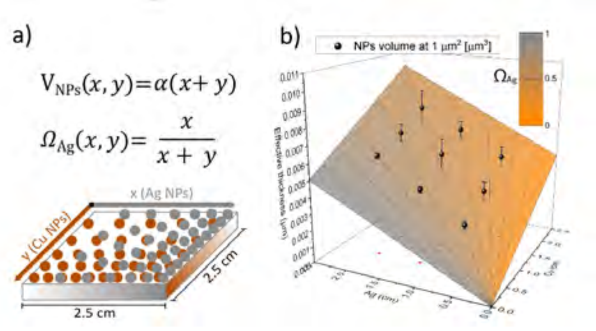

Figure 1. 2D two-metal NPs density linear gradient: (a) analytical description by V_{NPs} and Ω_{Ag} functions together with gradient illustration, (b) experimental measurements of V_{NPs} by SEM microscopy (dots with error bars), which were fitted by equations for linear gradient (wired surface denotes V_{NPs} and Ω_{Ag} is shown as colormap).

Acknowledgments

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Soldering wear of PVD coatings for HPDC tools for Al-alloys

Pal Terek[1*], *Lazar Kovačević*[1], *Aleksandar Miletić*[1 2], *Branko Škorić*[1], *Janez Kovač*[3], *Aljaž Drnovšek*[3], *Peter Panjan*[3]

[1]University of Novi Sad, Faculty of Technical Sciences, Trg Dositeja Obradovića 6, Novi Sad, 21000, Serbia
[2]Polytechnique Montreal, Department of Engineering Physics, Montreal, Quebec H3T 1J4, Canada
[3]Jožef Stefan Institute, Jamova 39, Ljubljana, 1000, Slovenia
[*]E-mail: palterek@uns.ac.rs

Keywords: high pressure die casting, aluminium alloy, PVD coating, surface roughness, soldering

High pressure die casting (HPDC) is used for mass production of complex, near-net shape and thin walled components of light alloys. Due to the ever-increasing application of light-weight materials in different products, application of HPDC is also progressively expanding. To improve production efficiency, one has to reduce HPDC tool soldering wear. Nowadays, this is usually accomplished by application of ceramic coatings produced by physical vapor deposition (PVD) on tool surfaces. Future development of non-sticking, soldering resistant PVD coatings requires fundamental knowledge about these specific processes, which are also influenced by surface roughness. Considering that information on this topic in literature is quite limited, we performed the following investigation. We evaluated the performance of duplex CrN and TiAlN PVD coatings prepared to different degrees of surface roughness. Soldering and corrosion behaviour in Al–Si–Cu cast alloy was evaluated by ejection test, performed with conventional (CS) and delayed cast alloy solidification (5 and 20 min) (DS). This test simulates a casting process and ejection of die core from a casting. The force required for ejection is a measure of cast alloy soldering toward pin material. After the tests, sample surface morphologies and chemical compositions were analysed by different microscopy and analytical techniques. For both coatings it was found that ejection force in CS experiments increase with decrease in surface roughness. Such increase is a consequence of two processes. The one is the reduced stress concentration underneath a casting surface during pin ejection, and the other is the enhanced cast alloy adhesion to smooth surfaces under tangential stresses. On the other side, ejection force for both coatings, substantially decreased in DS experiments (from 20 to 50%). Such decrease is observed for the whole range of investigated surface roughness. This effect is explained by mild coatings oxidation and formation of a thicker oxide scale in the casting. Casting scale forms due to the reduction of oxidised CrN layer by Al contained in cast alloy, which may be classified as diffusion wear. So far, such decrease of the ejection force, caused by oxidation of nitride coatings, is not reported in literature. These findings can be employed in design of non-sticking nanolayer coatings for HPDC tools. On sample surfaces, built-up layers with different morphology were distinguished. Based on the origins of their formation they were classified in two groups. The first group involved the effects of mechanical soldering, such as cast alloy built-up in front of nodular defects, agglomerations inside grinding marks and crater defects. These effects are observed on samples subjected to both experiments. The second group, comprised the effects of metallurgical soldering such as cast alloy sticking, oxidised casting scale and corrosion through coating defects. These effects are detected only on samples from DS experiments.

Effects of mechanical soldering are not detrimental to coating integrity but can reduce the tool efficiency and endanger casting and tool integrity. On the other side effects of metallurgical soldering, induce severe coating wear and eventually coating complete failure.

Acknowledgments

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T5: Surface Science

Raman scattering enhancement of silicon by photonic nanojet of a microsphere

Vlatko Gašparić[1], István Rigó[2], Davor Ristić[1], Hrvoje Gebavi[1], Miklós Veres[2], Mile Ivanda[1]*

[1]Research Unit New Functional Materials, Center of Excellence for Advanced Materials and Sensing Devices, Ruđer Bošković Institute, Bijenička cesta 54, 10000 Zagreb, Croatia
[2]Department of Applied and Nonlinear Optics, Wigner Research Centre for Physics, Konkoly-Thege Miklós út 29-33, 1121 Budapest
[*]E-mail: ivanda@irb.hr

Keywords: optical microsphere, photonic nanojet, Raman scattering, GLMT, SERS

A new method for enhancing the Raman scattering signal has emerged recently, based on dielectric enhancement. Especially promising is the dielectric method based on microspheres and photonic nanojet – a narrow highly concentrated beam of light on the shadow side of the irradiated microsphere. The formation of the photonic nanojet is presented through Generalized Lorenz-Mie theory (GLMT), together with important properties and applications. Simulation images of the photonic nanojet are shown, both as solutions of GLMT equations, and numerical simulations. Furthermore, the photonic nanojet is presented as Raman scattering enhancement method different substrates (bulk, film on bulk, etc.) with microspheres and microspheres with a stem. The variation of the incident beam position is discussed, where raw enhancement reaches highest value (5.7x) for 0.50 NA objective, when the incident beam was focused 9 µm below the top of the 5-µm microsphere. Moreover, the combined dielectric enhancement with metallic surface-enhanced Raman scattering (SERS) is presented, together with future plans.

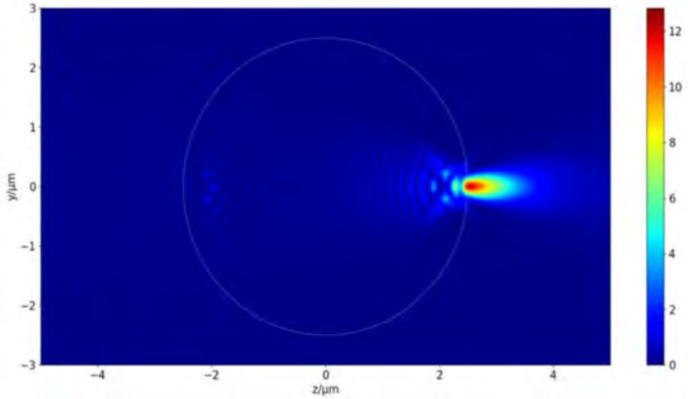

Figure: GLMT calculation of the photonic nanojet produced by irradiating a microsphere with a Gaussian beam of normalized intensity.

Acknowledgments
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Mechanical properties of single crystalline α-Al_2O_3 grown by chemical vapour deposition

Fabian Konstantiniuk[1*]*, Nina Schalk*[1]*, Michael Tkadletz*[2]*, Christina Kainz*[1]*,*
Christoph Czettl[3]

[1]Christian Doppler Laboratory for Advanced Coated Cutting Tools at the Department of Materials Science, Montanuniversität Leoben, Franz-Josef-Straße 18, 8700 Leoben, Austria
[2]Department of Materials Science, Montanuniversität Leoben, Franz-Josef-Straße 18, 8700 Leoben, Austria
[3]CERATIZIT Austria GmbH, Metallwerk-Plansee-Straße 71, 6600 Reutte, Austria
[*]E-mail: fabian.konstantiniuk@unileoben.ac.at

Keywords: CVD, α-Al_2O_3, micromechanical tests, EBSD

Due to the highly anisotropic mechanical properties of α-Al_2O_3, the lifetime of α-Al_2O_3 coated cutting tools is strongly influenced by its texture. However, limited literature is available on orientation dependent mechanical properties of α-Al_2O_3. Thus, in the present study, (0001), (11-20) and (1-102) oriented single crystalline α-Al_2O_3 coatings were synthesized using chemical vapour deposition (CVD) on sapphire substrates and the mechanical properties were investigated. The morphology of the coatings was studied by scanning electron microscopy and the respective orientation verified by electron back-scatter diffraction. Hardness and Young´s modulus of the differently oriented coatings were evaluated by nanoindentation, yielding the highest values of 34.6 ± 2 GPa and 452.1 ±15 GPa, respectively, for the (0001) oriented coating. Furthermore, micromechanical tests were carried out to determine the fracture stress and fracture toughness, where again the (0001) oriented coating exhibited the maximum values of 10.1 ± 0.6 GPa and 6.1 ± 0.4 MPa $m^{1/2}$, respectively. The results obtained within this work may serve as a valuable basis for the further development of α-Al_2O_3 coatings.

Structural evolution of bridge CO sites on Pt(111) surface studied by high resolution electron energy loss spectroscopy

Teng Ma[1*], *Zun Liu*[1], *Mengyao Zhang*[1], *Yaqin Wang*[1, 2*]

Institute of Science, Shenyang Agricultural University, Shenyang, P. R. China
School of Environmental and Chemical Engineering, Shenyang Ligong University, Shenyang, P. R. China *E-mail: tengma77@gmail.com (T.Ma) , m15802436358@163.com (Y.Wang)

Keywords: HREELS, vibrational frequency, bridge CO, structural evolution

CO adsorption on Pt and its alloys has been studied intensively for several decades, which is still of some mystery. Recently, the structural evolution of CO adsorption sites on Pt(111) has been achieved with more details: On Pt(111) above 50 K, bridge CO is found usually in the c(√3×2)rect unit of 4 top CO and 1 bridge CO molecules. Furthermore, the c(√3×2)rect unit could be presented in more structures in UHV, even embeded in the boundaries of local (√3×√3)R30°islands of top CO molecules. However, for the vibrational frequency of bridge CO molecules, there is a turning point around the c(4×2) superstructure with equal quantity of top and bridge CO molecules. In this report, by using HREELS, we studied the vibrational features of CO molecules adsorbed on Pt(111) around 107 K and found that there is a linear dependence between the vibrational frequency and the logarithm of CO exposure (L) at certain ranges. In reference to other reports, the evolution of frequency could be correlated well with the structural features. The c(√3×2)rect unit evolves from the dispersed one or two units to one dimensional in [1-10] and further to two dimensional c(4×2). After that, the c(√3×2) rect unit begins to become less ordered in [1-10], or prefers to hold one dimensional in [11-2] during conversion to the c(√3×5). In conclusion, the vibrational frequency of bridge CO molecules is dependent on both the density of c(√3×2)rect unit and its long-range order in [1-10] and [11-2].

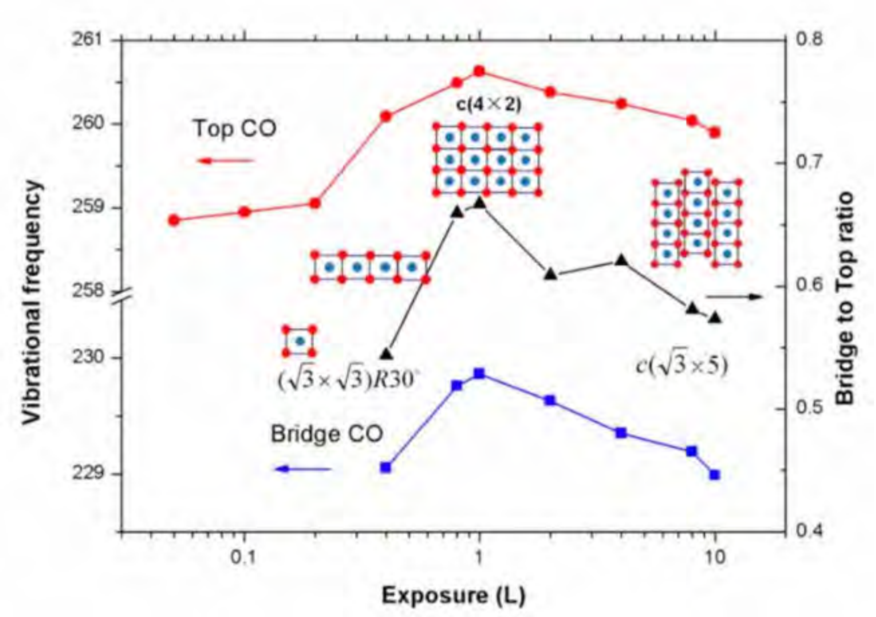

Figure1. Vibrational frequencies of top and bridge CO molecules with different exposures at 107 K

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Adsorption of azobenzene on hexagonal boron nitride nanomesh supported by Rh(111)

Ádám Szitás[1], *Richárd Gubó*[1,2], *Tibor Pásztor*[3], *Arnold Péter Farkas*[2,3], *Tibor Ajtai*[2,4], *László Óvári*[2,3]*, *Krisztián Palotás*[3,5], *András Berkó*[3], *Zoltán Kónya*[1]

[1]Department of Applied and Environmental Chemistry, University of Szeged, Szeged, Hungary
[2]Extreme Light Infrastructure – Attosecond Light Pulse Source, ELI-HU Non-profit Ltd. Szeged, Hungary
[3]MTA-SZTE Reaction Kinetics and Surface Chemistry Research Group, University of Szeged, Szeged, Hungary
[4]Department of Optics and Quantum Electronics, University of Szeged, Szeged, Hungary
[5]Institute for Solid State Physics and Optics, Wigner Research Center for Physics, Budapest, Hungary
*E-mail: ovari@chem.u-szeged.hu

Keywords: hexagonal boron nitride, h-BN, nanomesh, Rh(111), azobenzene, template effect, molecular switch, adsorption, STM, DFT, charge transfer, molecule-molecule interaction

The discovery of the fascinating properties of graphene, including its self-supporting nature and exceptional electronic properties solicited vivid interest in other two dimensional (2D) materials as well. Atomically thin hexagonal boron nitride (h-BN) has also been thoroughly investigated [1]. It is isostructural and isoelectronic to graphene, but the difference in electronegativity results in an insulating character with an electronic band gap of about 6 eV. In this work the adsorption properties of azobenzene – the prototypical molecular switch – was investigated on a periodically undulating h-BN monolayer (“nanomesh”) prepared on Rh(111). The h-BN layer was produced by decomposing borazine ($B_3N_3H_6$) at 1000-1050 K. Temperature programmed desorption (TPD) studies revealed that azobenzene molecules adsorbed on the “wire” and “pore” regions desorb at slightly distinct temperatures. Angle resolved high-resolution electron energy loss spectroscopy (HREELS) measurements demonstrated that the first molecular layer is characterized predominantly by an adsorption geometry with the molecular plane parallel to the surface. Scanning tunneling microscopy (STM) indicated a clear preference for adsorption in the pores, manifesting a templating effect, but in some cases one-dimensional molecular stripes also form, implying attractive molecule-molecule interaction. Density functional theory (DFT) calculations provided further details regarding the adsorption energetics and bonding, and confirmed the experimental findings that the molecules adsorb with the phenyl rings parallel to the surface, preferentially in the pores, and indicated also the presence of an attractive molecule-molecule interaction.

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Fabrication and chemical reactivity of nanoholey h-BN monolayer supported on Rh(111) surface

Tibor Pásztor[1*], *László Szabó*[2], *Barbara Bicsák*[2], *László Óvári*[1,3], *András Berkó*[1], *Zoltán Kónya*[1,2]

[1]MTA-SZTE Reaction Kinetics and Surface Chemistry Research Group, University of Szeged, Rerrich Béla. tér 1, H-6720 Szeged, Hungary
[2]Department of Applied and Environmental Chemistry, University of Szeged, Rerrich tér 1, H-6720 Szeged, Hungary
[3]ELI-ALPS, ELI-HU Nonprofit Ltd., Dugonics tér 13., H-6720 Szeged, Hungary
[*]E-mail: pasztortibor@chem.u-szeged.hu

Keywords: hexagonal boron-nitride monolayer, Rh(111), Ar-ion treatment, fabrication of nanoleaks and nanoflakes, scanning tunnelling microscopy, chemical reactivity, graphene, benzene, ethene, intercalation.

The “bottom up” formation of ultrathin 2D (graphene-like) materials on different metal supports has opened the way to study and modify systematically these materials with surface science techniques during the last two decades [1]. The application field of these new materials is very wide from the electronics and sensorics to the next generation environmental chemistry and energetics. Recently, an enhanced interest manifests for both the in-plane (lateral) and the parallel-plane (vertical) hetero structures of the 2D materials. In the frame of these research activities, the hetero structure of graphene (GR) and hexagonal boron-nitride (h-BN) is an exceptionally important case. The *parallel hetero structures* consisting of GR on h-BN exhibits special physical phenomena like integer and fractional quantum Hall effects, Coulomb drag, magnetic focusing [2] and chemical phenomena like the enhanced photoelectrocatalytic hydrogen generation [3]. The studies on graphene/h-BN *lateral hetero structure* are quite rare up to now, in spite of the very interesting phenomena appearing at the 1D phase borderline like special chemical activity and large magnetic moments [4].

In this work we present a procedure consisting of low energy (0.5 keV) Ar ion sputtering followed by annealing in ultrahigh vacuum at 1050 K for fabrication of h-BN nanosheets containing tailored nanoholes (diameter of 5–20 nm) on Rh(111) surface. First, a complete h-BN nanosheet was fabricated by chemical vapour deposition of borazine as it was described previously [5]. After the formation of nanoholes, we studied the chemical reactivity of the perimeters of the holes in the reaction with different molecular precursors like benzene (C_6H_6) and ethene (C_2H_4) applied for the formation of graphene flakes inside and outside around the h-BN nanoholes by scanning tunnelling microscopy (STM). Special attention was paid to the spill-over and intercalation phenomena at the perimeter sites of the h-BN nanoholes during their filling up with graphene layer.

Acknowledgments

The financial support of the National Research Development and Innovation Office of Hungary (K120115 and FK124100) is gratefully acknowledged.

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Focus on SIMS for the characterization of thin film devices

Nimer Wehbe[*]

Imaging and Characterization Core lab, King Abdullah University of Science & Technology (KAUST), Thuwal 23955-6900, Saudi Arabia
[*]E-mail: nimer.wehbe@kaust.edu.sa

Keywords: SIMS, depth-profiling, multilayer devices

Dynamic Secondary Ion Mass Spectrometry (D-SIMS) is a very powerful tool for the characterization of solid surfaces and is a requisite technique for researchers developing devices in the field of semiconductors, photovoltaics and energy storage technologies. Dynamic SIMS instruments equipped with quadrupole analyzer are simple and easy to use although they don't allow the best performance in term of mass resolution and sensitivity compared to SIMS instruments equipped with analyzers of magnetic sector type.

Throughout this contribution, I will be showing several examples obtained in our lab and illustrating the information that can be derived from the SIMS data [1,2]. The presentation will cover the most common topics requested by the researchers including the in-depth analysis of solar and photovoltaic cells, the in-depth quantification of elements incorporated either as dopant (SIMS) or as high content (SNMS). The presentation will be also focused on the characterization of multilayer devices and the limitation or artifacts that may be occurring during the sputtering process.

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T6: Thin film growth mechanism and models, new approaches

Microstructure evolution of equiatomic CrFeCoNiCu alloy thin films during in-situ TEM heating

Mohamed Arfaoui[1,2*], *György Radnóczi*[1], *Viktória Kovács Kis*[1,3]

[1]Centre for Energy Research of the Hungarian Academy of Sciences, Konkoly-Thege M. u. 29–33, H-1121 Budapest, Hungary
[2]Department of Physics, Eötvös Loránd University, Pázmány Péter sétány 1a, H-1117 Budapest, Hungary
[3]Institute of Environmental Sciences, University of Pannonia, Egyetem str. 10, H-8200 Veszprém, Hungary
[*]E-mail: Mohamed.arfaoui@mfa.kfki.hu

Keywords: multi-principal element alloy, in-situ TEM annealing, thermal stability, diffusionless transformation, oxide formation

Recently, bulk and thin film multi-principal element alloys (MPEA) have gained significant attention due to their promising thermal, mechanical and corrosion properties [1]. These alloys generally crystallize in single phase solid solution and undergo phase transformations [2]. In this study the MPEA 50 nm thick film of equiatomic CrFeCoNiCu alloy was subjected to in-situ TEM heating up to 700°C in the electron microscope. The pressure in the microscope during the whole annealing process was $6x10^{-7}$ mbar. The temperature was raised by 50 ^{o}C in each five minutes. Morphology and phase changes were in-situ recorded to track the early, intermediate and final stages of phase separation. Post annealing analysis of the redistribution of the composing elements was also measured.

The film was structurally and morphologically stable single phase FCC (a=3.60Å) solid solution up to 400 °C. At 450 °C the formation of a BCC phase (a=2.94Å) was observed, however, the morphology of the film remained unchanged. This type of transformation is attributed to diffusionless processes (martensitic or massive). The separation of the components sets in above 550 °C. Accordingly, fast morphological and structural changes started at this temperature. At 600°C fast growing of a new intermetallic phase was observed, containing mainly Cr and had a large unit cell of 2×2×4 of the bcc unit cell. The surface of the films got covered with a CrO-type oxide layer of lattice parameter 4.20 Å, possibly contributing to corrosion resistance of these films.

Acknowledgments

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On the origins of stress in polycrystalline thin films: a possible contribution of impurity effects via catalytic interactions

P.B. Barna[1], J.E. Greene[2], I. Petrov[2], G. Radnóczi[1]*

[1]Centre for Energy Research, Institute of Technical Physics and Materials Science,
Konkoly-Thege M. u.29-33, H-1121 Budapest, Hungary
[2]Materials Research Laboratory and Department of Materials Science, University of Illinois, Urbana,
Illinois 61801
*E-mail: barna.peter@energia.mta.hu

Experiments have generally demonstrated that in polycrystalline thin films both the nature (tensile or compressive) and the variation of the magnitude of the intrinsic stress developing during growth, are very sensitive to the preparation parameters. In this way, intrinsic stress can also be controlled. Analysis of the experimental results published in the literature demonstrate the effect of deposition rate and residual gas pressure on the stress evolution and initiated the idea that environmental impurities or additives (primarily CO and O_2) can affect and control the stress evolution. This is what the present contribution attempts to do by considering possible catalytic interactions on the surface of the growing crystals as a fundamental process. This is based on the fact that the catalytic effect, the promoted decomposition or formation of complexes, is linked mainly to defect sites (vacancies, monolayer steps, kinks) present on the surface of the crystals. As the defect sites are permanently reproduced during crystal growth, the surface of the growing film is a very active catalyst. Thus, by facilitating the dissociation of CO and CO_2 via the catalytic effect, C atoms can form and accumulate simultaneously on the growth surface. The C atoms can be incorporated as excess atoms into the crystal lattice, may accumulated at grain boundaries, or can even form a solid 2D or 3D carbon or carbide phases. These processes can modify the tensile stress developing when adjacent islands snap together to form new grain boundaries or create compressive stress. However, other catalytic processes must be also considered investigating the effect of increasing oxygen pressure. This is the oxidation of C and CO by oxygen producing CO_2 which easily desorbs and will be evacuated by the vacuum system.

A promising view based on possible catalytic processes will be proposed. It may allow a more comprehensive analysis of the complex phenomena of stress evolution, observed in experiments. In the framework of this view it is possible to interpret in a direct way the double effect of increasing oxygen pressure, published in the literature, when initially the tensile stress increases, then decreases and changes to compressive.

Hard alloy films with enhanced resistance to cracking

Zuzana Čiperová[1*], *Jindřich Musil*[1,2]

[1]Department of Physics and NTIS – European Centre of Excellence, University of West Bohemia, Univerzitní 22, CZ – 306 14 Plzeň, Czech Republic
[2]Institute of Physics v.v.i., Academy of Sciences of the Czech Republic, Na Slovance 2, CZ – 18221 Praha 8, Czech Republic
[*]E-mail: ciperovz@kfy.zcu.cz

Keywords: magnetron sputtering, alloy films, mechanical properties, resistance to cracking, hard films

The work reports on the mechanical properties of alloy films prepared by magnetron sputtering. It is known that alloy films easily crack due to a low ratio $H/E^* < 0.1$ [1,2]; here H is the hardness and E^* is the effective Young's modulus of the film. Cracking is a great drawback of alloy films as it strongly limits many of their practical applications. Therefore, it is important to develop new advanced alloy films with high hardness and enhanced resistance to cracking and that is the subject of the present investigation. It is shown that hard alloy films resistant to cracking must exhibit a high ratio $H/E^* \geq 0.1$, elastic recovery $W_e > 60\%$, compressive macrostress ($\sigma < 0$) and dense, voids-free microstructure. Deposition conditions under which such alloy films can be formed are given and mechanical properties of the Si-based hard alloy films with enhanced resistance to cracking are provided as examples.

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In situ TEM study of κ→β and κ→γ phase transformations in Ga_2O_3

Ildikó Cora[1], Zsolt Fogarassy[1], Roberto Fornari[2,3], Matteo Bosi[3], Aleksander Rečnik[4], Béla Pécz[1]*

[1]Centre for Energy Research, Institute of Technical Physics and Materials Science, Budapest, Hungary
[2]University of Parma, Dept. of Mathematical, Physical and Computer Sciences, Parma, Italy
[3]IMEM-CNR, Parma, Italy
[4]Department for Nanostructured Materials, Jožef Stefan Institute, Ljubljana, Slovenia
[*]E-mail: coraildiko@gmail.com

Keywords: Ga_2O_3, HRTEM, in situ phase transformation

The temperature-driven phase transformation of metastable κ-Ga_2O_3 layers[1] deposited on sapphire was studied by high resolution TEM. Annealing experiments up to 1000°C were performed either in situ in vacuum within the TEM or ex situ in ambient air[2]. This allowed for the detection of the atomistic mechanisms at the basis of κ to β phase transition. In the case of in situ TEM observations we could even record in real time the atomic rearrangement. We provide in this paper the relevant crystallographic relations between original κ and new β lattice.

Surprisingly, the ex situ experiments demonstrated the additional formation of a γ-Ga_2O_3 intermediate phase at 820°C. The remarkably different behaviour between in situ and ex situ annealing experiments is explained in terms of ambient (ambient air or high vacuum) and heating rate.

An extensive investigation of γ-Ga_2O_3, also a metastable phase, showed that it has a cubic defect spinel structure (F*d*-3*m*) with disordered vacancies. Repeated observations of the metastable γ-Ga_2O_3 after two months show that the vacancies tend to order, and that the vacancies are fully ordered after one year.

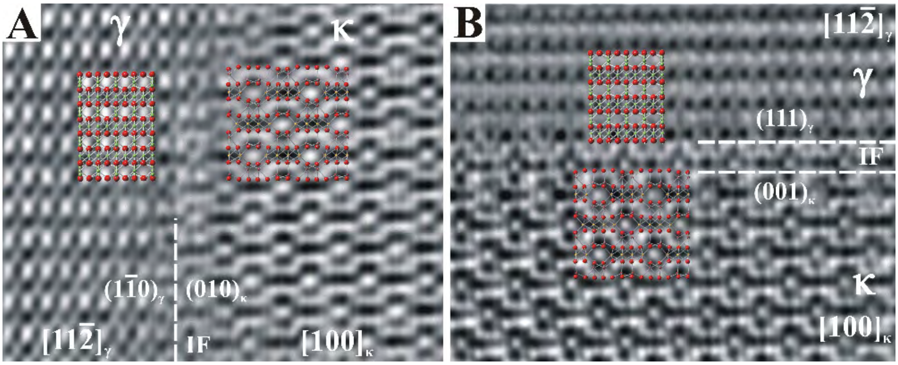

Figure 1. Fourier-filtered experimental HRTEM images of the κ→γ transformation with zig-zag lateral (**A**) and sharp vertical (**B**) interfaces in the thin film annealed *ex situ* up to 820°C.

Acknowledgments

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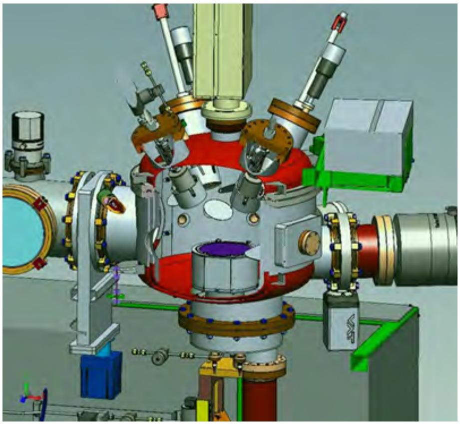
Structure and mechanical properties of hard and fracture tough WBC coatings

Zsolt Czigány[1*], *S. Mirzaei*[2], *M. Alishahi*[2], *P. Soucek*[2], *L. Zábransky*[2], *V. Buršíková*[2],
M. Stupavská[2], *V. Peřina*[3], *K. Balázsi*[1], *P. Vašina*[2]

[1]Institute of Technical Physics and Materials Science, Centre for Energy Research, Budapest, Hungary
[2]Department of Physical Electronics, Faculty of Science, Masaryk University, Brno, Czech Republic
[3]Nuclear Physics Institute, Academy of Sciences of the Czech Republic, Řež, Czech Republic
[*]E-mail: czigany.zsolt@energia.mta.hu

Keywords: TEM, hardness, ductility, nanocomposite, magnetron sputtering

The main challenge in deposition of protective coatings is to produce films which simultaneously exhibit high hardness and enhanced fracture toughness. Materials exhibiting such seemingly contradictory combination of mechanical properties – high hardness and moderate ductility – were already realized experimentally in Mo_2BC and recently predicted by ab-initio calculations in crystalline X_2BC system (X = Ti, V, Zr, Nb, Mo, Hf, Ta, W). Our aim is to produce fracture tough WBC protective coatings and to produce the theoretically predicted W_2BC crystalline phase. However, low formation enthalpy of W_2BC phase and existence of WB and WC phases to replace W_2BC phase indicate difficulties to deposit crystalline W_2BC films. The WBC films were deposited by combination of DC magnetron sputtering of W and B_4C targets and pulsed DC sputtering for C in Ar at a substrate temperature of 500ºC (Fig. 1). The pulsed regime resulted in 2.5 times increase of ion flux at 350 kHz and 65% duty cycle compared to DC sputtering. The bonding structure and mechanical properties were investigated by XPS and nanoindentation, respectively. Structural properties were investigated by TEM (including HRTEM and SAED) using a JEOL3010 and an aberration corrected Themis equipment. The films are mainly amorphous but contain nanocrystallites of ~5nm in the vicinity of the composition range of W_2BC. A certain level of short range ordering can be observed even in the amorphous films in the form of curved and irregular lattice fringes in HRTEM images. All the layers exhibited high hardness (>20GPa) so they all can be classified as hard coatings. The mechanical properties are mainly determined by the fraction of W-B bonds. WBC multilayers were also deposited in an industrial chamber (Fig. 2).



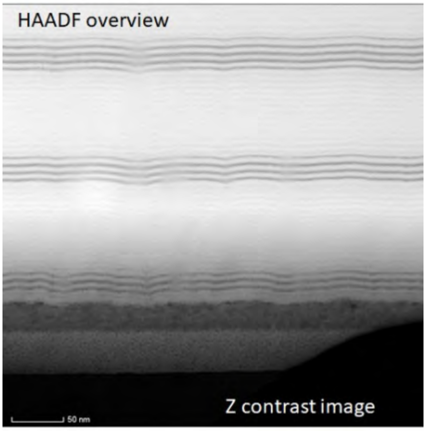


Figure 1. Schematic view of the deposition chamber with sputter sources.

Figure 2. HAADF image showing compositional variation in a WBC film deposited in an industrial chamber forming a multilayer structure.

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Reactions between amorphous thin films of silicon with nickel on heating

Erzsébet Dodony[1], György Z. Radnóczi[1], István Dódony[2]*

[1]Center for Energy Research, Institute of Technical Physics and Material Sciences,
Thin Film Physics Laboratory, Budapest, Hungary
[2]Department of Mineralogy, Eötvös Loránd University, Budapest, Hungary
*E-mail: dodony.erzsebet@energia.mta.hu

Keywords: thin film, nickel-silicide, crystal structure, electron crystallography

Controlled formation of nickel silicide materials is still extensively researched, due to their impact in microelectronics. As the industry is heading towards ever smaller device sizes, new challenges arise. The phase formation and sequence of the nickel silicides differ from the results of the bulk experiments, because of the restricted dimensions. In order to make and optimize devices and their performance, it is a must to know how the used materials are formed, what is their atomic structure, and how it transforms as a function of elapsed time.

In this work we present a study of a Ni-Si thin film model structure, with the focus on the development and structure of the $Ni_{31}Si_{12}$ - γ phase. The samples – 10nm thick a-Si foils, supported by a Ni microgrid – were heated in-situ to temperatures up to 600 °C, and the silicide formation was investigated (Fig. 1). The model structure was created by DC magnetron sputtering a layer of Si in Ar on cleaved NaCl substrate, then the a-Si layer was transferred to the Ni microgrid by dipping the NaCl in water. The grid acted as the metal source for the silicide formation, where the phases were identified through selected area diffraction (SAED) patterns and high-resolution transmission electron microscopic (HRTEM) images. We have observed multiple polymorphs of the $Ni_{31}Si_{12}$ - γ phase, and aimed to determine their crystal structure using techniques of electroncrystallography. The good match between simulated and the gathered experimental data validated the new crystal structures in the $Ni_{31}Si_{12}$ composition.

Figure 1. Sample after heating – with Ni microgrid on the left and a-Si on the right with silicide phases in between.

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Hydrogen formation in Radio Frequency (RF) sputtered hydrogenated silicon nitride thin films

Nikolett Hegedüs[1,2*], *Riku Lovics*[2], *Miklós Serényi*[2], *Zsolt Fogarassy*[2], *Péter Petrik*[2], *Judith Mihály*[3], *Zsolt Zolnai*[2], *Csaba Balázsi*[2], *Katalin Balázsi*[2]

[1]Doctoral School on Materials Sciences and Technologies, Óbuda University, Budapest, Hungary
[2]Institute for Technical Physics and Materials Science, Centre for Energy Research, Budapest, Hungary
[3]Centre for Natural Sciences, Budapest, Hungary
[*]E-mail: nhegedus@guardian.com

Keywords: hydrogenated silicon nitride, thin films, radio frequency sputtering

Hydrogenated silicon nitride thin films (Si_3N_4:H) have widespread application from device passivation to light emitting diodes and antireflective coatings for solar cells. The most common deposition techniques are different types of chemical vapor deposition methods. However, these techniques differ at several points. The deposited film always contains hydrogen. On the other hand, its amount can´t be controlled directly during the preparation process. Due to this fact, sputtering techniques could be interesting as alternative fabrication methods for controlled hydrogen concentration in direct way from zero by adjusting the applied hydrogen gas flow to the chamber.

In this work, hydrogen-free and hydrogenated silicon nitride films were deposited by Radio Frequecy (RF) sputtering applying various amount of hydrogen gas. Optical properties were investigated as a function of hydrogen concentration of the plasma. Structural characterization revealed that the porosity of the film can be significantly influenced by hydrogenation (Figure 1). Thermal stability and chemical composition were also studied with special regard to the hydrogen incorporation form in the films.

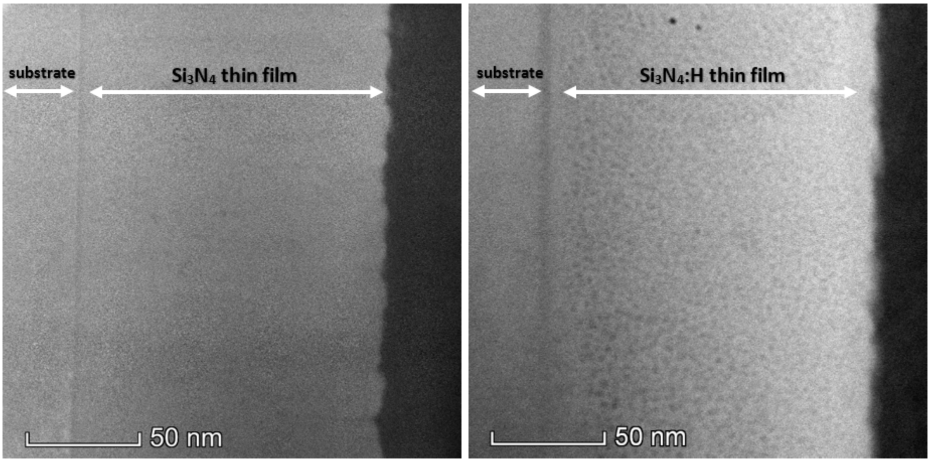

Figure 1. Transmission Electron Microscopy (TEM) image of hydrogen-free (left) and hydrogenated (right) silicon nitride thin films.

Effect of the relative Al to Cu Content in AlCuMgZn Multi-Principal Element Alloys

Johannes Kirschner[1], Georg Rasinger[1], Christoph Eisenmenger-Sittner[1], Johannes Bernardi[2], Clemens Simson[3]*

[1]Institute of Solid State Physics, Vienna Technical University, Wiedner Hauptstrasse 8-10, 1040 Vienna, Austria
[2]USTEM, Vienna Technical University, Wiedner Hauptstrasse 8-10, 1040 Vienna, Austria
[3]LKR Leichtmetallkompetenzzentrum Ranshofen, Lamprechtshausener Str. 61, 5282 Ranshofen, Austria
[*]E-mail: johannes.kirschner@tuwien.ac.at

Keywords: magnetron-sputtering, multi-principal element alloys, crystallography, light metal alloys

The development of new materials and alloys, particularly in the field of light metals, is a critical aspect in many technical areas, from the construction of more energy-efficient mobility solutions to the design of mechanically more robust alloys. Multi Principal Element Alloys (MPEAs) demonstrate great potential in this field and a challenge as well. Previous studies have shown that certain quaternary and quinary alloys, which contained approximately equal amounts of their constituents, outperformed conventional alloys. For the prediction of compatible elements and their optimal composition, especially in the field of light metals, there is a lack of reliable models and concepts.

Multi-component layers (thickness of 10 μm) were co-deposited by magnetron sputtering to reveal the complex correlation between chemical compositions, crystallography, mechanical properties and morphology. Al, Cu, Mg and Zn were chosen to investigate the effects of concentration changes on the crystal structure. For this purpose, the relative ratio of Al to Cu was flipped from Al dominated to Cu dominated in the AlCu compound. Subsequently, strong binary systems (namely $AlCu_2$ and Al_2Cu) were mixed with another stable binary system, $MgZn_2$ to investigate the effects of an additional binding partner. The aim was to find the concentration at which the established crystallographic phases disappear or merge. Special attention was paid to the effect of Cu on the microstructure.

By changing the relative position of the material sources and the substrate a broad compositional range could be scanned. Subsequent heat treatment resulted in a state of equilibrium of the samples.

A comparison between the Al-dominated and Cu-dominated systems was carried out by means of X-ray diffraction. We showed that Cu is mainly responsible for the formation of new crystallographic phases and the associated degeneration of the binary crystal systems. Furthermore, electron microscopic investigations showed phase separation and possible segregation of the constituents. This finding underlined the results obtained with XRD.

In order to gain insight into the mechanical properties, hardness measurements were carried out. The crystallographic properties were compared with mechanical properties and a non-trivial behaviour was found, depending on the modification of the binary crystal systems.

Acknowledgements

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Transrotational crystal growth in thin amorphous films revealed by TEM – basis for novel lattice-rotation nanoengineering

Vladimir Kolosov

Institute of Natural Sciences and Mathematics, Ural Federal University, Ekaterinburg, Russia
E-mail: kolosov@urfu.ru

Keywords: amorphous films, crystal growth, TEM, transrotational microcrystals, nanoengineering

Exotic thin crystals with unexpected **transrotational nano**structures [1] have been discovered by transmission electron microscopy (TEM) for crystal growth in thin (10-100 nm) amorphous films of different chemical nature (oxides, chalcogenides, metals) prepared primarily by vacuum evaporation methods. We use TEM bend-contour method [2] with HREM, AFM added in due cases.

The unusual phenomenon often can be traced in situ in TEM column during local e-beam heating or annealing: regular internal bending (dislocation independent) of crystal lattice planes in a growing crystal. Such **transrotation** (**trans**lation of the unit cell is complicated by small **rotation** realized round an axis lying in the film plane) can result in strong regular lattice orientation gradients (up to 300 degrees/μm) of different geometries: cylindrical, ellipsoidal, toroidal, saddle, etc., Fig.1

The possible mechanism of the phenomenon is discussed. Initial amorphous state and surface nucleation of the crystal growth are most essential factors. The last fact accompanied by anisotropy of crystal growth rate and tendency for regular change of interatomic distances of the crystal propagating from the surface layers inside the bulk resembles specific epitaxy, “vacuum epitaxy”, Fig.1d. Transrotation phenomenon is the basis for novel lattice-rotation nanoengineering of functional, smart thin-film materials with some features suitable also for strain nanoengineering. Transrotational micro crystals have been eventually recognized by different authors in some thin film materials vital in applications, e.g. phase change materials (PCM) for memory [3-4]. New model for the amorphous thin-film state is proposed, Fig.1e.

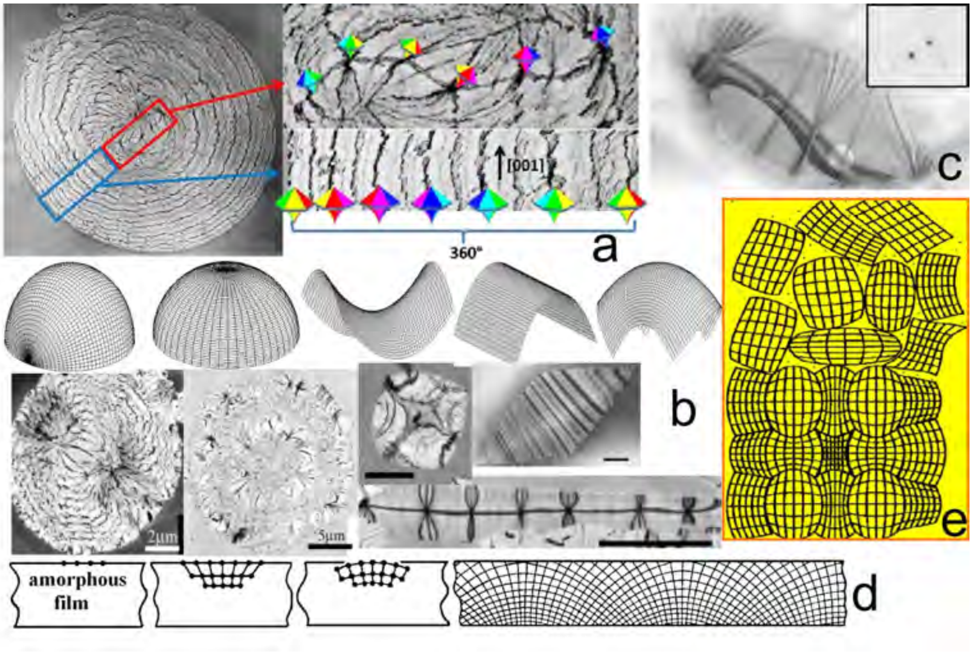

Figure 1. TEM of thin crystals grown in different amorphous films (**a**: Se-Te, **b**: Se, α-Fe_2O_3, Ta_2O_5, C+Se and $Cu_{2-x}Te$ below, **c**) with lattice curvature shown (**a** – in colors, **b** – geometry of lattice plane curvature and **c** - transrotation evidence supported by series of SAED), model for "vacuum epitaxy" in X-section (**d**), amorphous mixcrocrystalline model with transrotational grains (**e**).

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Theory of multicomponent crystal growth due to chemical reaction

Alexey Redkov[*], *Sergey Kukushkin*

Institute for Problems in Mechanical Engineering, Saint-Petersburg, Russia
[*]E-mail: avredkov@gmail.com

Keywords: multicomponent, crystal, growth, theory

Despite the fact that silicon is still one of the main materials for electronics, multicomponent crystals and films are being used in technology more and more. Widebandgap semiconductors like AlN, GaN, SiC are the basement for new generation of effective optoelectonic devices, LEDs, transistors. Complex crystalline compounds like perovskites $CH_3NH_3PbX_3$ (where X=I, Br and/or Cl) are good candidates for being used in solar cells. Moreover, increasingly sophisticated methods are emerging for the growth of such crystals and thin films, involving different chemical reactions. This gradual transition to new, more complex materials and methods require modification of the currently available theory to describe the growth of multicomponent crystals.

The aim of this work is to expand some of the existing models [1–3] for different crystal growth regimes onto multicomponent systems with chemical reactions and to find in general case analytical expressions connecting growth conditions (flows, reagent pressures), crystal properties and its growth rate. It is shown that equations describing the growth of a multicomponent crystal due to chemical reaction [1] are practically the same as for a classical single-component growth derived by Burton, Cabrera and Frank [4], but differ in parameters used. Some peculiarities of this process are discussed: namely formation of islands of individual components on crystalline surface during growth, and a dependence of the growth rate on absolute pressures of chemical reagents even at fixed supersaturation.

Acknowledgments

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Insight into the structural evolution during TiN film growth via atomic-resolution TEM

Zaoli Zhang

Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Leoben, Austria
E-mail: zaoli.zhang@oeaw.ac.at

Keywords: TiN nanocrystalline film, HRTEM, EELS

The appropriate substrate bias assists the formation of TiN coatings, and restricts the initiation of impurities and defects in the materials, resulting in the microstructural evolution during film growth, however, how the atomic-resolution structure of TiN films changes with the bias voltage remains unclear.

Here, the atomic-scale structures of the TiN films were intensively investigated with the high- resolution transmission electron microscope (HRTEM) from two viewing directions (plan-view and cross-sectional), complemented by X-ray photoelectron spectroscopy measurements, electron energy loss spectroscopy (EELS) and density functional theory (DFT) calculations.

Except for the significant changes of microstructure with different bias voltages, e.g., columnar grain evolution, grain size and dislocation density increase, voids and pores vanishing, extensive atomic resolution observations further exhibit that low-angle grain boundaries dominate the boundaries between two neighboring grains with zone axis [111] in the case of floating bias potential conditions. A high number of sub-grains comprised of dislocations can form in the films under certain bias conditions. Surprisingly, numerous twins are observed in the TiN films under some bias voltage conditions. The initiation of twins in TiN films can be essentially ascribed to the reduction of stacking fault energy (SFE) caused by non-stoichiometry to a certain degree, i.e., N/Ti atomic ratio. This has been corroborated by theoretical calculations. Moreover, observed atomic-scale structural characteristics (i.e., the variation of N/Ti atomic ratio) could reasonably account for the hardness alterations under different bias-voltages. Furthermore, the electronic structure subtlety triggered by bias-voltage changes is also revealed by the fine structure analysis. A correlation of atomic-scale structure with the mechanical property of films is also shown.

Acknowledgments

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T7: Thin film multilayer and superlattices

Investigation of the Fe-Ti interface asymmetry by Mössbauer spectroscopy

Judit Balogh[1], László Bujdosó[1], Gergő L. Hegedűs[1], Dénes Kaptás[1], László F. Kiss[1], Dániel G. Merkel[1], Akio Nakanishi[2], Dénes L. Nagy[1]*

[1]Wigner Research Centre for Physics, Budapest, Hungary
[2]Department of Physics, Shiga University of Medical Science, Shiga, Japan
*E-mail: balogh.judit@wigner.hu

Keywords: interface, alloy formation, Mössbauer spectroscopy

In a structurally perfect and chemically sharp layered structure it is only two monolayers of Fe atoms at the interface which "feel the presence of other kind of atoms", since hyperfine parameters of the Mössbauer atom are basically determined by atoms located in its first two coordination shells even in case of metallic systems. This allows us to reveal differences in width and chemical composition of the bottom and top interfaces of nanoscale Fe layers. For this purpose the Mössbauer parameters of equal Fe layer thickness Ti/Fe/Ti and Ti/Fe/Ag trilayer pairs are compared. (The layer sequence is given as starting from the bottom, i.e. from the substrate side.) The Mössbauer parameters of the Fe-on-Ti interface can be derived from the Ti/Fe/Ag samples, since the Ag-on-Fe interface is chemically very sharp and the Mössbauer parameters of two monolayers of Fe atoms at the Fe-Ag interface are well known from the literature. The Mössbauer parameters of the Ti-on-Fe interface can be derived from the comparison of the Ti/Fe/Ti and Ti/Fe/Ag sample pairs, as the fitted parameters and the intensity of the different components are compared. For example, if the bottom and top interfaces of the Fe layer are similar, then the hyperfine parameters of the Fe-Ti interface components remain unaltered and the intensity of sub-spectrum belonging to the interface is halved when the top Ti layer is replaced by Ag.

Applying the above method the asymmetry of the Fe-on-Ti and Ti-on-Fe interfaces predicted by molecular dynamics simulations has been approved experimentally [1]. Further on, the asymmetric interfaces of the as-received samples can be shown to result in different evolution of the phase compositions at the two interfaces under heat treatments below 300 °C. Here we point to the possibility that the asymmetric interface properties can lead to very different magnetic properties in sequence permutated multi-trilayers, as shown in Figure 1. The magnetic properties were investigated in details by SQUID magnetization measurements.

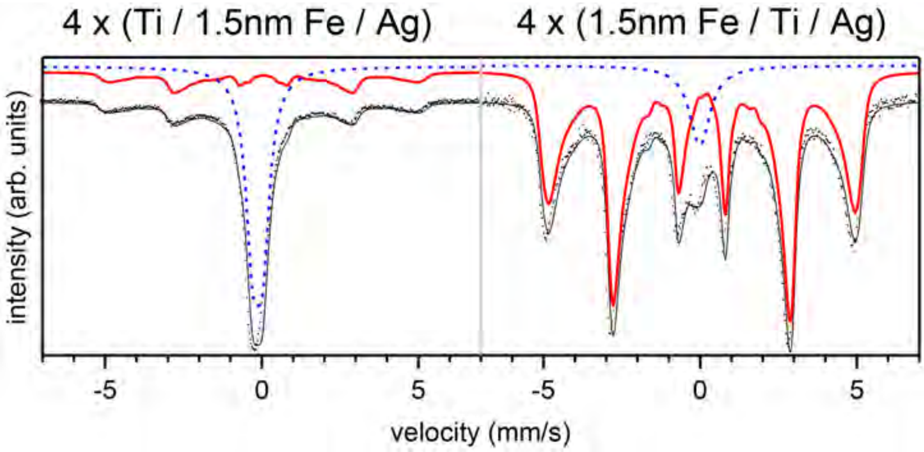

Figure 1. Room temperature Mössbauer spectra of Fe-Ti-Ag multilayers with different layer sequence; Si/10nm Ag/4x(15nm Ti/1.5nm Fe/15nm Ag) to the left; Si/10nm Ag/4x(1.5nm Fe/15nm Ti/15nm Ag) to the right. Black lines show the overall fitted spectra, while blue and red lines show the paramagnetic and ferromagnetic components, respectively.

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Prediction of composition and crystalline structure of sputtered multi-component coatings by a Virtual Machine

David Böhm[1*]*, Thomas Schrefl*[2]*, Andreas Eder*[3]*, Christoph Eisenmenger-Sittner*[1]

[1]Vienna University of Technology, Wiedner Hauptstrasse 8-10, 1040 Vienna, Austria
[2]Danube University Krems, Viktor Kaplan Str. 2 E, 2700 Wiener Neustadt, Austria
[3]MIBA High Tech Coatings GmbH, Dr.-Mitterbauer-Str. 3, 4655 Vorchdorf, Austria
[*]E-mail: david.boehm@tuwien.ac.at

Keywords: sputtering, co-sputtering, thin film multilayer, thin film composite material, sputter-simulation, simulated film growth, XRD diffractogram calculation, XRD measurement

To be able to predict the composition and the structural properties of multi-component thin films deposited by magnetron sputtering a so-called Virtual Machine (VM) was designed. The VM is an interactive ray tracing software that simulates film growth by a line-of-sight model, also taking into account the decay of the flux density of the particles due to gas phase scattering.

The VM is initiated with a 3D model of a real sputter system which includes the static arrangement of multiple targets and the substrate and eventual obstacles, as well as dynamics like e. g. rotating substrate holders. Then the composition and the crystallographic phases with their associated XRD patterns are calculated for the simulated film. On each sampling point a composition is calculated over several time steps associated with an adjustable temperature which can be different for each step enabling the correlation of the real temperature distribution during the coating experiment.

With this information and a library of binary phase diagrams the corresponding crystallographic phase can be calculated and displayed per time step. The XRD patterns are calculated from the crystallographic phases and summed over all time steps. This procedure allows constructing a diffractogram which can be compared to the diffractogram of an accordingly produced sample. Another way to display the data is to stack the appearing composition and phases over all time steps. Such a phase stack is equivalent to an EDX line scan performed on a metallurgical cross section from the substrate to the surface of the coating. Several phase stacks can be compared with an element mapping of the cross section. Since surfaces and volume diffusion are not yet considered, only immiscible multilayer systems can be investigated at present. On the basis of examples the above mentioned comparisons are presented.

Acknowledgments

This project has received funding from the Clean Sky 2 Joint Undertaking under the European Union's Horizon 2020 research and innovation program under Grant No. 785414

T8: Semiconductor, dielectric & piezoelectric thin films

In situ TEM study of kinetics of Ag-induced crystallization of amorphous Ge films

Aleksandr Kryshtal[1*], *Sergiy Bogatyrenko*[2], *Paulo Ferreira*[3]

[1]Faculty of Metals Engineering and Industrial Computer Science & International Centre of Electron Microscopy for Material Science, AGH University of Science and Technology, Poland
[2]School of Physics and Technology, Karazin National University, Kharkiv, Ukraine
[3]Iberian International Nanotechnology Laboratory, Braga, Portugal
[*]E-mail: kryshtal@agh.edu.pl

Keywords: metal-induced crystallization, in situ HR (S)TEM, phase transformations, metastable phases, nucleation, EELS

Low-temperature crystallization of amorphous semiconductor films (Si, Ge) in contact with a metal (e.g, Au, Ag, Al, Bi, Pd) is commonly referred to as "metal-induced" or "metal-mediated" crystallization (MIC). Despite numerous studies of the MIC effect, a fundamental mechanism of the reaction is still an issue. In this work, we have applied advanced electron microscopy techniques for studies of the initial stages of the reaction in Ag-Ge couple.

Self-supported Ag-Ge films were used as a model, ensuring a true binary system free of substrate-induced stresses. The films were formed at room temperature on KCl single-crystal cleavages by the sequential deposition of Ge and Ag at a pressure of $5 \cdot 10^{-8}$ Torr. The bimodal ensemble of Ag particles (ca. 7 and 40 nm in size) on an amorphous and continuous Ge film (10 nm thick) was formed. Synthesized Ag-Ge samples were separated from the substrate and were transferred on through-hole MEMS-based chips for in situ TEM investigation.

The nucleation and growth of the crystalline Ge phase were observed at the atomic scale in real-time by heating the system in a Cs corrected FEI Titan 60–300 in the 20–450°C temperature range. Ag and Ge plasmon resonance peaks were used for chemical mapping of elements at different stages of the reaction without substantial radiation damage of the area under study. HAADF-STEM tomography was applied for 3D reconstruction of post-annealed Ag/Ge film structure.

We found that the crystallization process is activated by large Ag nanoparticles, while small ones were completely inert at any temperature studied. Eutectic nucleus was formed at the metal-semiconductor interface at temperatures well below the eutectic temperature of the bulk alloy, and it triggers the crystallization of the amorphous Ge film. The excess energy of the amorphous Ge drives the formation of liquid and the propagation of the reaction front through the Ge film, which results in the crystallization of the entire Ge film. Intermetallic Ag-Ge hcp compound was identified at the reaction front, which is due to the solidification of the non-equilibrium liquid alloy at the reaction zone.

Acknowledgments
We acknowledge funding from the National Science Centre, Poland under Grant No. 2016/23/B/ST8/00537. Part of the study has received funding from EU Horizon 2020 research and innovation program under grant agreement No. 823717_ESTEEM3.

Fabrication of progressive devices for microwave photonics

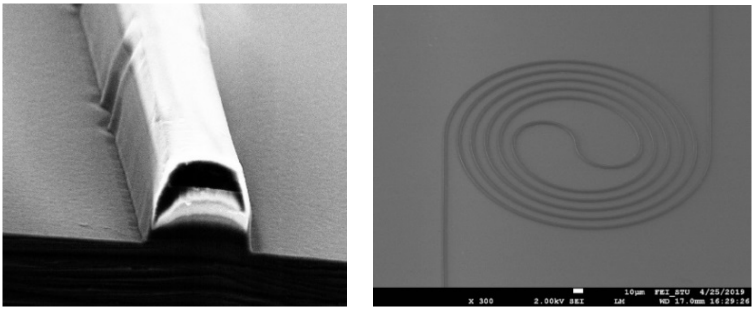
Ľuboš Podlucký[1*], *Jozef Chovan*[2], *Jaroslav Kováč jr.*[1,2], *Marián Vojs*[1], *František Uherek*[1,2]

[1]Faculty of Electrical Engineering and Information Technology, Slovak University of Technology,
Ilkovičova 3, 812 19 Bratislava, Slovakia
[2]International Laser Centre, Ilkovičova 3, 841 04 Bratislava, Slovakia
[*]E-mail: lubos.podlucky@stuba.sk

Keywords: silicon oxynitride, PECVD, ICP/RIE, microwave photonics, waveguide

Microwave photonics (MWP), a field that uses optical devices and techniques to generate, process, control and distribute high speed radiofrequency (microwave) signals, has been in the center of interest of the research community for the past 30 years [1]. The primary areas of use of the MWP are communication systems (cellular, wireless, and satellite), cable television, distributed antenna systems, optical signal processing and internet of things [2]. Integrated photonics not only makes it possible to reduce the footprint and complexity of MWP systems but offers much more. In the past years, the main monolithic materials used for wafer scale fabrication of integrated photonic devices have been III–IV (compound) semiconductors (InP, GaAs), element semiconductor (SOI – silicon-on-insulator) and dielectrics (silica and silicon nitride). Silicon oxynitride (SiON) is a promising candidate to serve as a core material of middle refractive index contrast integrated photonics. SiON waveguides with SiO_2 cladding have lower loss than other silicon-based waveguides [3].

We have investigated the deposition and etching of silicon oxynitride (SiON) layer for optical waveguides on silicon wafer. SiON layers were deposited using plasma-enhanced chemical vapor deposition (PECVD) system. Thickness, uniformity and refractive index was measured by micro-spot spectroscopic reflectometry and confirmed by ellipsometry. Surface roughness was measured by atomic force microscopy (AFM). Aluminum (Al) mask was fabricated for etching using lift-off process. SiON layers were etched in low pressure inductively coupled plasma – reactive ion etching (ICP-RIE) chamber using CF_4 gas. Scanning electron microscope (SEM) has been used to study the overall structure quality of SiON optical waveguide core. Etch rate has been optimized after several iterations to achieve a sufficient profile angle and micro trenching of resulting structures shown on Fig. 1.



a) b)

Figure 1. SEM images of ICP/RIE etched SiON (a) strip waveguide and (b) optical delay line.

Acknowledgments

The work was supported by Grant VEGA 1/0733/20 through the Ministry of Education, Science, Research and Sport of Slovakia, project APVV-17-0662 and APVV-16-0124 from Slovak research and development agency of Ministry of Education, Science, Research and Sport of the Slovak Republic

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T9: Magnetic, superconducting and multiferroic thin films

Characterization of magnetic properties of thin films by using magnetic field imaging based on colour centres in diamond crystal

Andris Berzins[1*], *Janis Smits*[1], *Roberts Rimsa*[2], *Gatis Mozolevskis*[2], *Andrejs Petruhins*[3]

[1]Laser Centre, University of Latvia, Latvia
[2]Laboratory of Prototyping of Electronic and Photonic Devices, Institute of Solid State Physics, Latvia
[3]Materials Design Group, Thin Film Physics Division, Department of Physics, Chemistry and Biology (IFM), Linkoping University, Sweden
[*]E-mail: andris.berzins@lu.lv

Keywords: magnetic field imaging, Nitrogen-Vacancy centres, optically detected magnetic resonance

Nitrogen-Vacancy (NV) centres in diamond crystal are well known for their capability to measure magnetic field distributions with high spatial resolution. When a thin layer of NV centers is located close to the surface of a diamond, magnetic field distributions created by microscopic magnetic field sources can be imaged at the position of the NV layer. In this work we present a method designed to measure magnetic properties of magnetic thin films and results from magnetic field imaging experiments (Fig. 1).

Strenght of magnetic field imaging method using NV centres in diamond crystal:

- The features of NV centres allow them to be used to image both magnitude and direction of magnetic field distributions with very high spatial resolution while maintaining good magnetic field sensitivity.
- Diamond matrix is mechanically and chemically resistant and has great thermal conductivity. Also NV centres in diamond allows flexible solutions for different problems (sensitivity and spatial resolution).

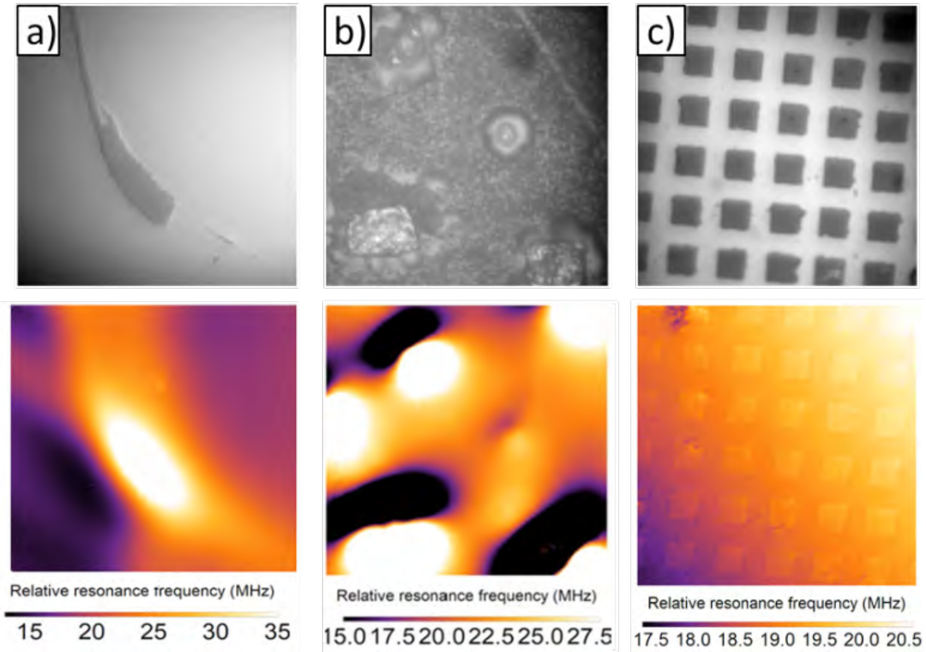

Figure 1. Images of different magnetic structures. Top row optical images, bottom row magnetic images, field of view 110x100 µm. a) mechanical defect on the surface of a 500 nm thick Fe thin-film; b) surface defects of a thin film made of $(Cr_{0,5}Mn_{0,5})_2GaC$, magnetic defects: Mn_5Ga_8 or Cr_5Ga_8, c) 10x10 µm squares made of 220 nm thick Cr_2O_3 above Neel temperature.

Acknowledgments

A. Berzins acknowledges support from PostDoc Latvia project 1.1.1.2/VIAA/1/16/024 "Two-way research of thin-films and NV centres in diamond crystal" and LLC "MikroTik" donation, administered by the UoL foundation, for opportunity to improve experimental set-up.

Investigation of phase transformations in Fe-Pt based thin films

Szilvia Gulyas[1], N.Y. Schmidt[2], A.P. Burmak[3], M. Albrecht[2], I.A. Vladymyrskyi[3], G.L. Katona[1]*

[1]Department of Solid State Physics, University of Debrecen, P.O. Box 400, H-4002 Debrecen, Hungary
[2]Institute of Physics, University of Augsburg, Universitätsstraße 1, D-86159 Augsburg, Germany
[3]Metal Physics Department, National Technical University of Ukraine
"Igor Sikorsky Kyiv Polytechnic Institute", Prospect Peremogy 37, 03056 Kyiv, Ukraine
[*]E-mail: gulyas.szilvia@science.unideb.hu

Keywords: magnetic thin films, solid state reactions, $L1_0$-FePt, $L1_0$-MnPt

In nanostructured films diffusion processes and solid state reactions often induce or take place by specific processes, which are not (or not significantly) observed in microcrystalline materials. The phases that appear during these processes are in many cases ordered. Since these phases influence the physical (eg, magnetic, electrical) properties of the materials, it is important to get in depth knowledge about the conditions under which they are formed in order to facilitate or even avoid their formation. We have investigated structural changes in DC magnetron sputtered Fe/Pt(/X) (X=Mn, Tb) thin films annealed in vacuum between 280–620°C. We investigated the structural properties and phase composition of the samples by x-ray diffraction (XRD) and also carried out chemical depth profiling by secondary neutral mass spectrometry (SNMS) in order to get information about the depth distribution of the elements. We have found that the addition of Mn and Tb significantly promoted the formation of the ordered phases.

In case of Mn addition the most prominent change at temperatures between 280-450°C was the formation of $L1_0$-MnPt at the interface of the Mn and Pt layer, along with the appearance of a metastable bcc Fe_3Pt phase. Further annealing lead to the transformation of the metastable bcc Fe_3Pt phase into fcc Fe_3Pt and finally into $L1_2$ Fe_3Pt. The final annealing at 620°C resulted in two phases: an antiferromagnetic $L1_0$-MnPt with addition of Fe and a ferromagnetic $L1_2$-Fe_3Pt.

Adding Tb as the third component also resulted in the intermixing of Pt and Tb after annealing at 215°C leading to the formation of the Pt_2Tb phase. After annealing at 280°C the A1-FePt chemically disordered phase appeared and significant Tb segregation (and oxidation) was observed. At 450°C the chemically ordered $L1_0$-FePt phase started to form and simultaneously the Pt_2Tb phase disappeared. At 620°C the final products are $L1_0$-FePt and TbO_2 phases.

T10: Thin films for optoelectronics, nanoelectronics, spintronics and batteries

Fabrication and characterization of electrochromic device combining NiO_x and WO_x thin films for controlling visible and near-infrared light

Chihiro Nakai[1], Yoshio Abe[1], Midori Kawamura[1], Kyung Ho Kim[1], Takayuki Kiba[1],*
Satoko Furukawa[2], Naoki Shirai[2], Kiyotaka Takeda[2]

[1]Kitami Institute of technology, Kitami, Japan
[2]Hokkaido Gas, Sapporo, Japan
[*]E-mail: m1952600132@std.kitami-it.ac.jp

Keywords: Electrochromic device, Nafion electrolyte, Ta_2O_5 protective film

Electrochromism is the phenomenon in which reversible color change of materials occurs by electrochemical reactions. Nickel oxide (NiO_x) and tungsten oxide (WO_x) are well known electrochromic (EC) materials. It is well known that NiO_x and WO_x show large transmittance changes in visible light and near-infrared regions, respectively. A complementary EC device using NiO_x and WO_x can modulate visible and near-infrared region simultaneously. Barawi, et al. [1] reported EC devices that can selectively control sunlight in visible and near-infrared. So in this study, we fabricated a device that can selectively control light in the 300 ~ 1100nm region by combining two EC cells with NiO_x and WO_x EC layers.

NiO_x(200nm), WO_x(200nm) and Ta_2O_5(50nm) thin films were deposited by RF magnetron sputtering system. Ta_2O_5 was used to prevent the dissolution of NiO_x film into electrolyte. Nafion 20 wt% dispersion solution was used as an electrolyte. The structure of the fabricated cells are as follows:

(a) glass/ITO/NiO_x/Ta_2O_5/Nafion/ITO/glass, (b) glass/ITO/WO_x/Nafion/ITO/glass. A voltage was applied to each of the cell (a) and (b), and the transmittance of the EC device that stacked the cells (a) and (b) was measured using UV-visible spectrophotometer.

Fig.1 shows the transmittance spectra of the EC device. From the transmission spectra, four different transmittance states were realized. (1) Only WO_x was bleached, the device colored brown and transmittance of near- infrared (about 1000nm) region was high. (2) Only NiO_x was bleached, the device colored blue and transmittance of short-wavelength visible (about 500nm) region was high. (3) Both NiO_x and WO_x were bleached, the device was transparent and transmittance was high in all wavelength regions. (4) Both NiO_x and WO_x were colored, the device colored grayish blue and transmittance was low in all wavelength regions.

From these results, the fabricated device could realize four color patterns and control the transmittance in visible and near-infrared regions selectively.

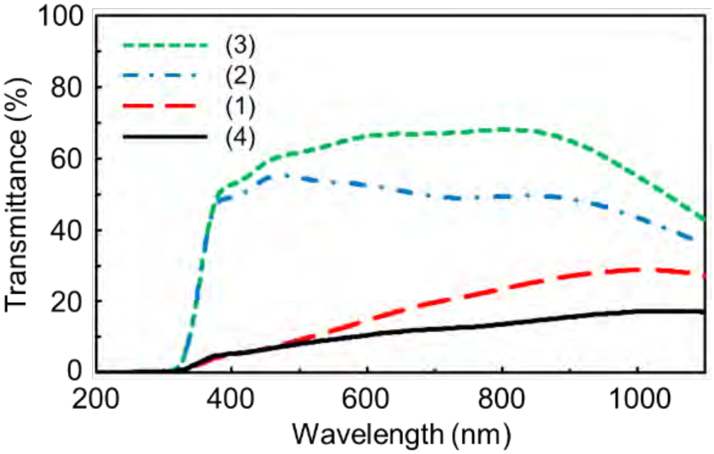

Figure 1. Transmittance spectra of the EC device.

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Transparent thermoelectric thin films for thermal energy harvesting applications

*J.M. Ribeiro[1], F.C. Correia[1], A. Kuzmin[2], I. Jonane[2], M. Kong[5], A. R. Goñi[5,6], J. S. Reparaz[5], A. Kalinko[3,4], E. Welter[4], C.J. Tavares[1]**

[1]Centre of Physics, University of Minho, 4710-057 Braga, Portugal
[2]Institute of Solid State Physics, University of Latvia, LV-1063 Riga, Latvia
[3]Department Chemie, Naturwissenschaftliche Fakultät, Universität Paderborn, Warburger Strasse 100, 33098 Paderborn, Germany
[4]Deutsches Elektronen-Synchrotron − A Research Centre of the Helmholtz Association, Notkestraße 85, D-22607 Hamburg, Germany
[5]Institut de Ciència de Materials de Barcelona-CSIC, Esfera UAB, 08193, Bellaterra, Spain
[6]ICREA, Passeig Lluís Companys 23, 08010 Barcelona, Spain
*E-mail: ctavares@fisica.uminho.pt; Telephone: +351 235 510474 (Corresponding author)

Keywords: thin films, TiO2:Nb, Seebeck, thermoelectric, EXAFS, sputtering

Transparent n-type niobium-doped titanium dioxide thin films (TiO_2:1.5 at.%Nb) with pronounced thermoelectric properties were produced from a composite Ti:Nb target by reactive magnetron sputtering. The thin films were comprehensively characterized by X-ray diffraction, X-ray photoelectron spectroscopy, optical spectroscopy, electrical conductivity, and thermoelectric measurement techniques. The local structure of the thin films was investigated in detail by X-ray absorption spectroscopy at the Ti and Nb K-edges. A set of radial distribution functions were extracted from the simultaneous analysis of EXAFS data at two absorption edges using the reverse Monte Carlo method. It was found that Nb dopant atoms modify the local environment of the films, but their average structure remains close to that of the anatase phase. This conclusion is also supported by the ab initio simulations of XANES. A very high absolute Seebeck coefficient ($S=155\ \mu V/K$) for n-type TiO_2 was achieved with Nb doping, yielding a maximum power factor and thermoelectric figure of merit of 0.5 $mW\cdot m^{-1}\cdot K^{-2}$ and 0.18 at a temperature of 300 K, respectively, for a 150 nm thick film. From frequency-domain thermoreflectance experiments, a thermal conductivity value of 1.3 $W\cdot m^{-1}\cdot K^{-1}$ was obtained for the optimized TiO_2:Nb film.

Effect of pressure and ageing on electrical properties of tin thin films

Shiva. L. Udachan[1*], *N.H. Ayachit*[2], *Udachan. L.A*[3], *Shivakumar Siddanna*[4],
Shrishail. S. Kolkundi[5], *Ramya S.*[6]

[1,2]Dept of Physics, Rani Channamma University, Belagavi-591156, Karnataka, India
[3]S. S. Tegnoor Degree College, Kalaburagi-585105, Karnataka, India
[4]Dept of PG Studies & Research in Physics, Kuvempu University Jnanasahyadri,
Shankaraghatta-577451, Shimoga, Karnataka, India
[5]Government First Grade College, Shahapur-585223, Yadgir, Karnataka, India
[6]Shree Sangam Vidya Mandir, Kalaburagi-585104, Karnataka, India
[*]E-mail: shivaudachan8@gmail.com

Keywords: tin films, pressure, ageing, electrical resistivity

Pressure happens to be one of the important deposition parameters which controls electrical and microstructural properties of tin films. Hence a systematic study is needed together information on effect of pressure and ageing effects. Tin films in the thickness range (40-160) nm were grown in a conventional vacuum coating unit. The conduction electron mean free path was greatly affected due to the change in pressure. Ageing effect on the tin nanofilms was studied. It reflects that an increase in the resistance was observed when the samples were exposed to the atmosphere with respect to time. The micro-structural study of tin films was carried using Atomic Force Microscope (AFM), Transmission Electron Microscope (TEM), Scanning Electron Microscope (SEM) and Energy Dispersive Spectroscopy (EDS) devices.

T12: Thin film sensors & actuaators

Organic vapour sensor based on oxidized nanostructured silicon surface

Nikola Baran[1,2], *Hrvoje Gebavi*[1,2], *Lara Mikac*[1,2], *Davor Ristić*[1,2], *Marijan Gotić*[1,2], *Kamran Ali Syed*[1,2], *Mile Ivanda*[1,2]*

[1]Laboratory for Molecular Physics and Synthesis of New Materials, Ruder Bošković Institute, Bijenička c. 54, 10000 Zagreb, Croatia; nikola.baran@irb.hr (N.B.), hrvoje.gebavi@irb.hr (H.G.), lmikac@irb.hr (L.M.), davor.ristic@irb.hr (D.R.), gotic@irb.hr (M.G.), kamran.syed@irb.hr (K.S.)
[2]Research Unit New Functional Materials, Center of Excellence for Advanced Materials and Sensing Devices, Bijenička c. 54, 10000 Zagreb, Croatia
*E-mail: mile.ivanda@irb.hr; Tel.: +385-1-456-0928

Keywords: porous silicon, gas sensing, thin film

Porous silicon has been intensely studied for the past several decades and its applications were found in photovoltaics, biomedicine and sensors. An important aspect for sensing devices is their long–term stability, in particular with respect to oxidation in the atmosphere. We have studied the influence of oxidation on sensing properties of porous silicon,and observed that electrical resistance of oxidized samples changes in response to the increasing ambient concentration of organic vapours and ammonia gas. Furthermore, we note the sensitivity is dependent on the oxygen treatment of the porous layer. This indicates a potential use of oxygen-treated PSi as a sensor for vapourized organic solvents and ammonia gas.

Acknowledgment

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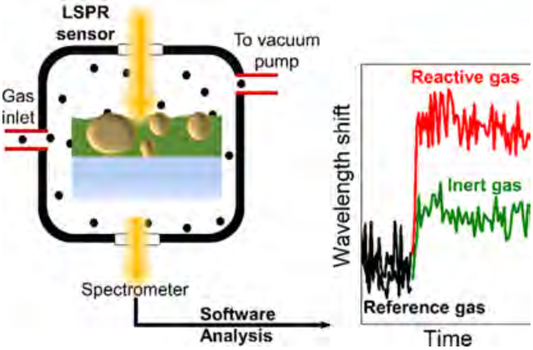
Nanocomposite thin films for gas sensing with high-resolution localized surface plasmon resonance spectroscopy

Manuela Proença, Marco S. Rodrigues, Joel Borges, Filipe Vaz*

Centro de Física das Universidades do Minho e Porto, Universidade do Minho, Braga, Portugal
*E-mail: joelborges@fisica.uminho.pt

Keywords: thin films, gold nanoparticles, localized surface plasmon resonance, gas sensing

Gas sensing, based on bulk refractive index (RI) changes, has been a challenging task for localized surface plasmon resonance (LSPR) spectroscopy [1]. In this work, it is demonstrated that a plasmonic thin film composed of Au nanoparticles embedded in an oxide matrix can be used to detect small changes (as low as 6×10^{-5} RIU) in bulk RI of gases at room temperature, using a High-Resolution LSPR spectroscopy system. Such thin film system was optimized by reactive magnetron sputtering, followed by an in-air annealing protocol to promote the Au nanoparticles growth [2,3]. A plasma treatment was used to enhance the sensitivity of the films, which exhibited high sensitivity to inert gases, presenting refractive index sensitivities to bulk RI changes of about 425 nm/RIU. Furthermore, a 2-fold signal increase was observed for oxidizing/reactive gases, showing that the thin film system is more sensitive to non-inert gases, due to chemisorption. The results showed that the nanoplasmonic thin film system is a RI sensitive platform able to detect inert gases, which can be more sensitive to detect non-inert gases as O_2 or even reactive gases.



Acknowledgments

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A multilayer Lead Oxide photoconductor for lag-free operation of X-ray digital detector

Oleksandr Grynko[1*], *Gytis Juska*[2], *Alla Reznik*[3,4]

[1]Chemistry and Materials Science Program, Lakehead University, Thunder Bay, ON, Canada
[2]Department of Solid State Electronics, Vilnius University, Vilnius, Lithuania
[3]Physics Department, Lakehead University, Thunder Bay, ON, Canada
[4]Thunder Bay Regional Health Research Institute, Thunder Bay, ON, Canada
[*]E-mail: ogrynko@lakeheadu.ca

Keywords: X-ray digital detector, Lead Oxide, photo-CELIV, charge transport, image lag

Lead Oxide (PbO) is one of the most promising candidates as a photoconductor for direct conversion digital X-ray detectors. Two polymorphic forms of Lead Oxide are considered for application: polycrystalline (poly-PbO) and newly developed amorphous (a-PbO). Due to the good photoconductive properties, thin layers of poly-PbO have a long history of utilization in optical imaging, in so-called “Plumbicon” video pick-up tubes. Thick poly-PbO layers were later used in the direct conversion X-ray detectors. However, they did not show adequate temporal behaviour for real-time applications due to image lag – residual signal after the termination of the X-ray pulse. Although the nature of the lag is still unclear, it is believed to be related to the peculiar structure of poly-PbO film – a network of individual long platelets oriented primarily in the growth direction. In contrast to poly-PbO, newly synthesized a-PbO layers are homogeneous, free of voids and show lag-free X-ray response. Although very promising, a-PbO layers are being developed to the point where an engineering solution must be applied to make PbO-based X-ray sensors. In this work, we engineered a bi-layer structure, where a thick poly-PbO film that acts as an X-ray–to–charge transducer was separated from the biased electrode with a thin lag-preventing layer of a-PbO. This allowed to maintain efficient charge transport while eliminating image lag. The holes’ transport was characterized at different temperatures and electric fields. Weak temperature dependence and strong dependence on the electric field of the holes’ mobility indicate dispersive transport that is governed by spatial inhomogeneity, similarly to what was previously observed in poly-PbO layer. However, in contrast to plain poly-PbO layers, X-ray exposure in pulsed mode shows nearly uniform signal amplitude with no build-up or degradation observed, even at a high frame rate. The reported approach to manufacture a multilayer detector allows to combine all the benefits of poly-PbO and a-PbO photoconductors and to overcome their drawbacks. The absence of image lag allows utilization of Lead Oxide photoconductor in the most demanding X-ray medical imaging procedures, such as fluoroscopy.

Acknowledgments

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Nanostructured WO_3 based bilayer thin films for hydrogen gas sensing

Stanislav Haviar[*], *Nirmal Kumar, Šárka Batková, Jiří Čapek*

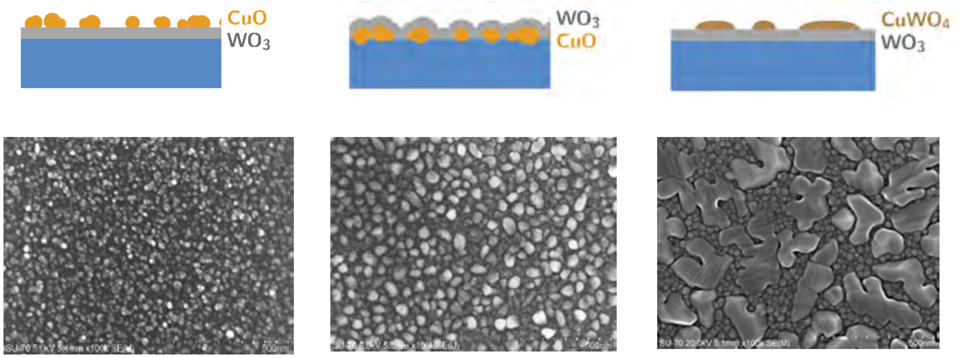
NTIS and Department of Physics, Faculty of Applied Sciences, University of West Bohemia, Pilsen, Czech Republic
[*]E-mail: haviar@ntis.zcu.cz

Keywords: nanoclusters, $CuWO_4$, WO_3, hydrogen sensing, heterojunction

In this study we demonstrate the advantages of two advanced sputtering techniques for preparation of thin film conductometric gas sensor. We combined tungsten trioxide (WO_3) thin films prepared by conventional reactive dc sputtering with (i) cupric oxide (CuO) nanoclusters deposited by gas aggregation cluster source (GAS) and (ii) with nanostructured copper tungstate ($CuWO_4$) layer prepared by reactive rf sputtering.

Both approaches enabled us to synthetize nanostructures with an enhanced conductometric sensorial response in comparison with WO_3 film alone. The prepared bi-layer films are depicted in Fig. 1. The enhanced response is explained by forming of nanosized electronic junctions. In case of CuO nanocluster, the *p*-*n* junction is formed, CuO is *p*-type semiconductor, WO_3 is *n*-type. The copper tungstate is *n*-type and so hetero *n*-*n* junction is formed.

Presented techniques create nanostructured sensing material without need of any wet process-steps nor sintering. This makes them suitable choices for integrating of nanostructured hydrogen sensors with microcircuits.



(a) (b) (c)

Fig. 1. SEM micrographs and schemes of investigated structures. (a) CuO clusters on the WO_3 film; (b) CuO cluster covered with WO_3 film; (c) $CuWO_4$ nanostructures on WO_3 thin film.

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T13: Vacuum Science & Technique

Preliminary electron desorption results of selected HL-LHC technical surfaces at cryogenic temperature

Michal Haubner[1*], *Vincent Baglin*[2], *Bernard Henrist*[2]

[1]Department of Physics, Faculty of Mechanical Engineering, Czech Technical University in Prague, Czech Republic
[2]European Organization for Nuclear Research (CERN), Geneva, Switzerland
[*]E-mail: michal.haubner@cern.ch

Keywords: electron stimulated desorption, dynamic vacuum, technical surfaces

CERN's Large Hadron Collider (LHC) is a 28 km circumference proton storage ring that mostly comprises of a 1.9 K UHV chamber embedded inside superconducting magnets. A beam-screen is used to shield the cold bore from the heat of synchrotron radiation and from an electron-cloud induced by the circulating bunched beam.

The electron-cloud irradiates the technical-grade copper surface of the beam-screen and desorbs gas under way. Hence, this electron-stimulated desorption (ESD) is the prominent gas source that may degrade the UHV in the beam-pipe and consequently decrease the beam life-time. Understanding of the ESD phenomena provides a vital link between the electron cloud and the associated dynamic vacuum effects, which recently gain importance in view of the High-Luminosity upgrade of the LHC (HL-LHC).

Typical operating conditions within the LHC beam-screen are controllably reproduced inside a recently designed experimental setup. Sample representative of beam-screen's copper surface is load-locked into a baked UHV chamber. Low energy and low intensity monochromatic electron beam is used to irradiate the studied sample and stimulate gas desorption. The ESD yield of each gas specie is proportional to its partial pressure rise, which is monitored online by a quadrupole mass spectrometer.

In this presentation, the commissioning and calibration procedure of this new setup and preliminary data on selected technical-grade materials is presented. The dependence of ESD on an electron energy and absorbed dose are discussed.

Acknowledgments
The corresponding author thankfully acknowledges the extensive support of CERN's TE-VSC group. This participation was supported by the Ministry of Education, Youth and Sports of the Czech Republic [Czech Technical University in Prague project SGS18/173/OHK2/3T/12].

Contamination propagation under high vacuum conditions: simulation and experimental study

Rudolf Schönmann[1,2*], *Hoai My Van*[1], *Gabriele Schrag*[1], *Gerhard Wachutka*[1], *Peter Ramm*[2], *Axel Müller*[3], *Wolfgang Mai*[3]

[1]Chair of Physics of Electrotechnology, Technical University of Munich, Munich, Germany
[2]Fraunhofer EMFT, Munich, Germany
[3]OHB System AG, Wessling, Germany
[*]E-mail: schoenmann@tep.ei.tum.de

Keywords: contamination, Monte Carlo simulation, free molecular flow, predictive simulations, experimental validation

In many applications, measurement equipment is or has to be operated under vacuum conditions, be it in the field of industrial manufacturing or research or space missions. In high vacuum environments, outgassing of contaminants can be a serious issue, since the re-deposited material might deteriorate the performance, or even lead to the total failure of the embedded equipment. Recording the contamination level by direct measurement often proves to be difficult and is not always technically feasible. Hence, the prediction of the contamination spread by computer-aided, physically-based simulations provides a viable alternative with a view to virtually prototyping such set-ups in conjunction with the consideration of quality assessment and assured long-term reliability. A particular challenge arises from the proper selection of the physical surface absorption/desorption models and the calibration of the relevant model parameters, as well as from the wide span of time-constants to be covered, when the long-term evolution of contamination processes shall be predicted as, e.g., it is required for assessing the reliability of components for space missions.

In order to tackle this challenge, we are going to develop a simulation tool based on the Monte-Carlo simulator Molflow+, which is currently validated and calibrated with reference to dedicated experiments [1]. The particle transport in vacuum is simulated using Molflow+, extended by a special model of the physical contamination process that describes the particle-surface interactions and generates the necessary physics-based parameters for the particle transport simulation. The particle-surface interactions are modelled using the residence-time approach as alternative to the commonly used sticking factors. According to Frenkel, the residence time is described as a function of temperature and binding energy, which in turn depends on the contamination level [2]. The evolution of the degree of contamination is then computed by iteratively solving the coupled equations governing transport and physical contamination. The code is made amenable to parallel computing, thus enhancing its numerical performance. Plausibility checks show a very good agreement between analytically calculated and simulated results for simple geometries.

However, to ensure the validity of the models, a comparison of simulated and experimental data of realistic, application-oriented situations is indispensable. Therefore, a measurement setup for characterizing the time-dependent propagation of water through a vacuum system is currently built up. By varying the temperature and the non-trivial geometry of the vacuum system, an extensive data set will be extracted and compared with simulated predictions, thus allowing for the tuning of the computer algorithms and the adjustment of the physical parameters. Measurement series and comparison to simulated data are on their way and will be presented at the conference.

In conclusion, we have developed a simulation tool for modelling the short- and long-term evolution of contaminations in vacuum systems based on the physical parameters temperature and binding energy. The simulation model is currently tested and tuned on the basis of experimental data.

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T14: Electronic Materials and Processing

Effects of fabrication dynamics on the current transport behaviour of Ag/p-$SnTe_xSe_{1-x}$ Schottky diodes

Naresh Padha[*], *Anjali Devi, Arun Banotra*

Department of Physics, University of Jammu, Jammu-180006, Jammu & Kashmir, India
[*]E-mail: nareshpadha@gmail.com

Keywords: Schottky diode, barrier height, ideality factor, hysteresis loop, current-voltage, capacitance-voltage, FTO glass, ITO polymer

The tin selenide (SnSe) material has been reported as an absorber layer of the solar cell structure. The undertaken $SnTe_xSe_{1-x}$ thin films are found to be a mixture of orthorhombic SnSe and hexagonal Te phases and exhibits Te-rich or SnSe-rich response depending upon the substrate temperature. These films are reported show 'bandgap (E_g)' tuning, moreover, their 'absorption coefficient (α)' value is higher and 'electrical resistivity (ρ)' is lower to SnSe. Further, the characteristics of $SnTe_xSe_{1-x}$ thin films vary with change in the substrate temperature. Thus, the $SnTe_xSe_{1-x}$ films turn up a suitable alternative to SnSe as absorber in the solar cell structure. The Schottky barrier interface of these semiconductors plays a vital role in their current transport behaviour. These contacts draw an insight into the bonding structures and defect levels in solids. The circular-shaped Ag/p-$SnTe_xSe_{1-x}$ Schottky barrier diodes (SBDs) were formed on FTO coated glass and ITO coated polymer substrates. The barrier heights of the SBDs formed on ITO coated polymer provide lower value than those formed on FTO glass. The variation in the BH values may be ascribed to the presence of additional microscopic asperities between the $SnTe_xSe_{1-x}$ semiconductor layer and ITO polymer. The double sweep I-V characteristics of FTO/p-$SnTe_xSe_{1-x}$/Ag schottky barrier diodes (SBDs) were measured for different delay times, the minimum hysteresis effect was observed at the step delay time of 5 ms. The values of ideality factor (η), series resistance (R_s) increase while zero bias barrier height (ϕ_{bo}) decreases with increase in the diameter. These variations in the 'η' and 'ϕ_{bo}' values may be due to increase in the 'surface defects' and presence of more number of 'low BH patches' at the MS interface which create inconsistencies in the current transport behaviour emanating from centre towards the radial directions. The ideality factors (η), series resistance (R_s) decrease whereas saturation current density (J_s) and barrier heights (ϕ_{bo}) increase with increase in substrate temperature of the deposited films. The variation in the current transport behaviour of the undertaken SBDs with substrate temperature are attributed to the alterations in the 'unit cell' parameters and 'strain' values of 'Te' and 'SnSe' lattices of $SnTe_xSe_{1-x}$. The higher values of capacitance (C) observed at low frequencies are attributed to the high dielectric values of the deposited films. Such a variation of capacitance values is attributed to the presence of more number of surface states (N_{ss}) and high relaxation time (τ). Further, the discrepancy in the I-V and C-V barrier heights may be explained on the basis of existence of an unintentional 'interfacial oxide layer' and 'trap states' present at the semiconductor surface.

T15: Nanometer Structures

Investigation of the thermally generated Au/Ag nanoislands for SERS and LSPR applications

István Csarnovics[1*], *Attila Bonyár*[2], *Miklós Veres*[3], *Petra Pál*[1], *László Balázs*[1], *Géza Szántó*[1], *Attila Csík*[4], *Laura Juhász*[5], *Sándor Kökényesi*[6]

[1]Department of Experimental Physics, University of Debrecen, Debrecen, Hungary
[2]Department of Electronics Technology, Budapest University of Technology and Economics, Budapest, Hungary
[3]Institute for Solid State Physics and Optics, Wigner Research Centre for Physics, Budapest, Hungary
[4]Institute for Nuclear Research,,Bem sq 18/c, 4026 Debrecen, Hungary
[5]Department of Solid State Physics, University of Debrecen, Debrecen, Hungary
[6]Department of Electrical Engineering, University of Debrecen, Debrecen, Hungary
[*]E-mail: csarnovics.istvan@science.unideb.hu

Keywords: gold nanoparticles, silver nanoparticles, localized surface Plasmon resonance, surface enhanced Raman scattering, plasmonics, nanosensing devices.

Gold and silver nanoparticles are widely used as signal amplification elements in various electrochemical and optical sensor applications. Although these NPs can be synthesized in several ways, perhaps one of the simplest methods is the thermal annealing of pre-deposited thin films on glass. With this method, the parameters of the annealing process (time, temperature) and the pre-deposited thin film thickness influence and define the resulting size and distribution of the NPs on the surface. Localized surface plasmon resonance (LSPR) is a very sensitive optical phenomenon and can be utilized for a large variety of sensing purposes. Surface-enhanced Raman spectroscopy (SERS) is an analytical method that can significantly increase the yield of Raman scattering of target molecules adsorbed on the surface of metallic nanoparticles.

In this work, the performance of Au/Ag nanoislands was investigated for SERS and LSPR applications. The nanoislands were generated by thermally annealing thin layers of silver and gold, which were previously sputtered onto glass surfaces. Pure metallic (silver and gold nanoparticles – AuNP and AgNP) system was evaluated based on their plasmonic and SERS sensitivity. Also the plasmonic sensitivity was simulated for gold and silver, nanocubes and nanospheres with the MNPBEM Matlab toolbox. The sensitivity of LSPR and SERS based devices are strongly depending on the used material, on the size and geometry of the metallic nanoparticles. By controlling these parameters the plasmon absorption band can be tuned and the sensitivity can be optimized. It was found that the enhancement factor depends on the size of the nanoparticles and on the distance between the particles. The efficiency can be maximized by increasing the nanoisland size, which can be achieved with a thicker starting layer, and by reducing the particle distance, which can be achieved by reducing the heat treatment time. Thus, in this case, the most important thing is to increase the specific surface area of the nanostructures, the density of the scattering centers.

Acknowledgments

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Designing embedded nanoparticle structures by ion-implantation

Gabriella Jáger[*], *János J. Tomán, Zoltán Erdélyi*

Department of Solid State Physics, University of Debrecen, Debrecen, Hungary
[*]E-mail: jager.gabriella@science.unideb.hu

Keywords: nanoparticles, ion-implantation, plasmonics, photonics, simulation, SKMF, segregation

Oxide thin films implanted with low-energy metal ions have attracted large attention due to their potential applicability in producing non-volatile memory, catalytical, optical and plasmonic devices. [1] In this study we show that for low-energy ion implantation the surface through which the implantation happened can have a significant influence on the formation of the embedded metal nanoparticles during annealing.

Using Stochastic Kinetic Modelling Framework (SKMF) [2-4] we performed atomistic computer simulations. In this work we present multiple processes through which the surface can affect the nanoparticle formation process significantly. We also show how this can be turned into an advantage as certain surface modifications after the ion-irradiation but before the annealing can be used as designing steps for the embedded nanoparticle structures.

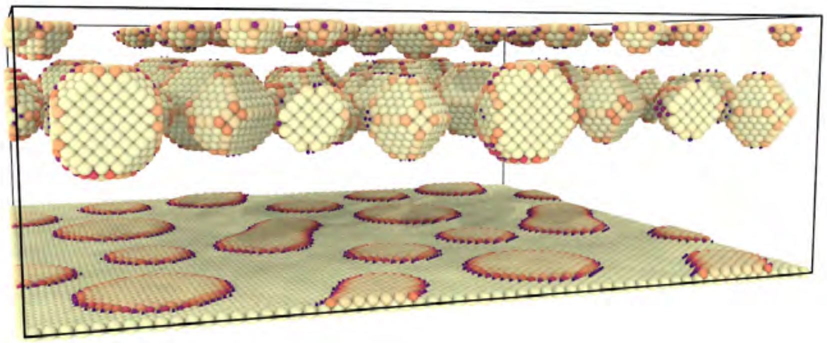

Figure 1. Formation of metal nanoparticles in oxide thin film during post-implantation annealing.

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How to tune the plasmon resonance frequency of porous gold nanoparticles?

Laura Juhász[1], Bence Parditka[1], Péter Petrik[2], Zoltán Erdélyi[1], Csaba Cserháti[1]*

[1]Department of Solid State Physics, University of Debrecen, Debrecen, Hungary
[2]Institute of Technical Physics and Material Science, Centre for Energy Research, Budapest, Hungary
[*]E-mail: cserhati.csaba@science.unideb.hu

Keywords: porous gold nanoparticles, atomic layer deposition, mixed metal-oxide coating, tunable localized surface plasmon resonance

Porous gold nanoparticles (PGNs) are very popular due to their high surface/volume ratio, moreover they have stronger plasmonic properties than their solid counterparts [1,2]. These properties makes porous gold nanoparticles advantageous for lots of applications (chemical sensors, cancer therapy applications, etc.). However, in application point of view it is indispensable that the resonance frequency (RF) of a plasmonic structure to be tunable. In this presentation we show that the RF can be adjusted in a wide range as desired by covering PGNs with metal-oxide layer. By changing the composition of the coating layer the RF can be shifted practically continuously in a wide range determined by the refractive index of the used oxides. As a demonstration, PGNs were coated with mixed alumina-titania oxide layers (5-7 nm) using plasma-enhanced atomic layer deposition method. The oxide layer, beside as a tuning tool, also passivates the morphology of PGNs when are exposed to elevated temperature. This is shown by the influence of the temperature (from 350°C up to 700°C) on the morphology, and as a consequence the optical extinction spectra of the oxide coated PGNs.

Acknowledgments

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Control of the localized surface plasmon resonance of Ag nanoparticles by changing its size and morphology

Takayuki Kiba, Kazuaki Masui, Yuuki Inomata, Midori Kawamura, Yoshio Abe, Kyung Ho Kim*

Department of Materials Science and Engineering, Kitami Institute of Technology, Kitami, 090-8507, Japan
*E-mail: tkiba@mail.kitami-it.ac.jp

Keywords: Ag nanoparticles, Ag thin films, thermal evaporation, localized surface plasmon

Recently, increasing the quantum efficiency of light emission by combining light emitter and metal thin films or nanostructures has been attracted much attention. In these studies, surface plasmon (SP) plays an important role in enhancing the light emission. SP resonance frequency of metal nanostructures can be controlled by changing its size and morphology. In this study, we fabricated the Ag nanoparticles (NPs) with different sizes by the annealing of the Ag thin-films with different thicknesses. The optical properties of the SP resonance of Ag NPs and the original Ag thin-films are investigated, and the emission enhancement properties combined with the organic emitter are examined.

Ag thin-films with thicknesses of 5, 10, 15, 20 and 25 nm are deposited by thermal vacuum evaporation on the quartz substrate. Subsequently, the obtained Ag thin-films are annealed at 400°C for 1 h on the hot-plate in the argon gas atmosphere. The morphology of the resultant Ag NPs is measured using scanning electron microscopy (SEM), and the obtained images are analyzed by ImageJ software. The organic emitter, tris(8-hydroxyquinolinato)aluminum (Alq_3) thin-films are overcoated on the Ag NPs Transmittance and reflectance spectra of the Ag NPs, and the photoluminescence spectra of Alq_3 with Ag NPs are measured.

As shown in Fig. 1 (a), the averaged diameters of the obtained Ag NPs are increased from 50 to 300 nm, as the thickness of the parent Ag thin-films increased. Corresponding to the size change, the significant red-shift of the absorption peak which can be assigned to the localized SP resonance of the Ag NPs, as shown in Fig. 1 (b). About 4-fold enhancement of the photoluminescence of Alq_3 was observed in combination with the proper size Ag NPs, which can be applied for the improvement of the light-extraction efficiency of the organic light-emitting devices.

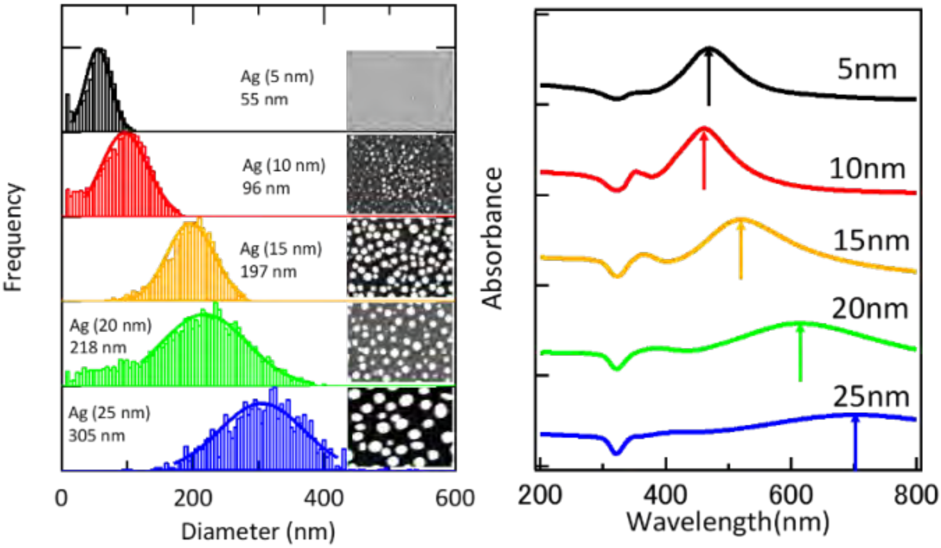

Figure 1. (a) Histograms of the size-distribution for Ag nanoparticles after annealing of the Ag thin films with each thickness at 400°C. Inset shows the SEM image of the Ag nanoparticles. (b) Absorption spectra of Ag nanoparticles with different sizes.

Acknowledgments

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Oxidation states of active catalytic centres in CO_2 hydrogenation on ceria based Ni catalysts: an XPS study

Ákos Szamosvölgyi[1], András Sápi[1,2], T. Rajkumar[1], Marietta Ábel[1], Imre Szenti[1], János Kiss[1,3], Juan Fernando Gómez-Pérez[1], Ákos Kukovecz[1], Zoltán Kónya[1,3]*

[1]University of Szeged, Interdisciplinary Excellence Centre, Department of Applied and Environmental Chemistry, H-6720, Rerrich Béla tér 1, Szeged, Hungary
[2]Institute of Environmental and Technological Sciences, University of Szeged, H-6720, Szeged, Hungary
[3]MTA-SZTE Reaction Kinetics and Surface Chemistry Research Group, University of Szeged, H-6720, Szeged, Hungary
[*]E-mail: szamosvolgyi@chem.u-szeged.hu

Keywords: transition metals, heterogeneous catalysis, CO_2 reduction, interface, solid solution, XPS

Catalytic CO_2 conversion is one possible way to make use of the anthropogenic CO_2 that is emitted into the atmosphere as waste. A promising method is to convert CO_2 chemically, to produce valuable feedstock materials (e.g. methane, methanol) for the chemical industry. While noble metals' excellent catalytic properties are undeniable, they are scarce and expensive materials, hence the research for noble metal free solutions is of great interest. To fully comprehend what phenomena play the key roles in a heterogonous catalytic system we must turn our attention to properties of the support materials or interfaces involved.

In this study the effect of interface and phase state are investigated in the case of CeO_2 based catalysts enhanced with NiO, which is added in the form of nanoparticles (interface) or lattice dopant (solid solutions state). These prepared catalysts were also compared to the pure Ce or Ni oxide samples. The synthesised materials were characterised with TEM, XRD, Raman spectroscopy, BET and H_2-TPR techniques. Reactions were run in a continuous flow test reactor attached to a GC equipped with TCD and FID detectors. *In situ* DRIFTS and *ex situ* XPS results were evaluated to comprehend reaction mechanisms.

Different Ni concentrations were tested for both types of catalysts, where Ce:Ni molar ratio was 99:1, 95:5 and 90:10. During CO_2 hydrogenation test reactions the samples containing the most Ni proved to have the highest consumption rate for both the interfacial and solid solution types, indicating the enhancing properties of the Ni. Comparing the catalytic behaviour of the interfacial mixed oxide and the solid solution we found the behaviour was significantly different in terms of product selectivity and conversion. The interfacial catalytic system converts 79% of the CO_2 feed, with a product selectivity of 97% favouring CH_4, opposed to the solid solution sample, which converts only 2% and promotes CO with 94% selectivity. With in situ DRIFTS we confirmed that both catalytic systems promote the formate pathway to form the products. During *ex situ* XPS the Ce 3d, Ni 2p and O 1s spectrum regions were analysed before and after reaction. Ce^{3+} and Ce^{4+} species were identified; the interfacial sample has a higher ratio of Ce^{3+}/Ce^{4+} indicating increased oxygen storage capacity thus it is more capable of chemisorbing and activating CO_2 before reaction. Thus it is capable of re-oxidizing the reduced NiO nanoparticles, creating a mixed oxide state by the end of the reaction cycle. However, the solid solution sample has less oxygen storage capacity, due to fewer lattice defects and less Ce^{3+}/Ce^{4+} ratio. The findings from ex situ XPS conclude, that the oxygen spill-over effect of ceria is of high importance regarding catalytic activity and in the case of solid solution ionic/oxidized Ni (Ni^{2+}) diffuses into the bulk of the sample.

Poster Presentations

T1: Applied Surface Science

Plasmonic response of thin films composed of noble metal nanoparticles dispersed in dielectric matrixes

Diogo Costa[1], Marco S. Rodrigues[1], Lucian Roiban[2], Thierry Epicier[2], Philippe Steyer[2], Joel Borges[1], Filipe Vaz[1]*

[1]Centro de Física das Universidades do Minho e Porto, Universidade do Minho, Campus de Gualtar, 4710-057, Portugal
[2]Université Lyon, INSA-Lyon, MATEIS UMR CNRS 5510, 21 Avenue Jean Capelle, Villeurbanne, Cedex, 69621, France
[*]E-mail: diogo.eccosta@gmail.com

Keywords: Localized Surface Plasmon Resonance, optical (bio)sensing, thin films, DC magnetron sputtering, Transmission Electron Microscopy

Plasmonic nanoparticles, such as Au and Ag, have been studied with the purpose of developing highly reliable, sensitive and label-free optical (bio)sensors. Characteristics of these nanoparticles, like size, distribution, shape and composition, can greatly affect the absorption band that arises from Localized Surface Plasmon Resonances. This effect is also found in magnetron sputtered thin films, composed by noble metal nanoparticles embedded in dielectric matrixes, and it is possible to change the optical properties of the of LSPR band of these thin films using post-deposition annealing. This thermal treatment induces changes in the morphology and crystallinity of both the matrix and the noble metal, promoting the formation of nanoparticles and altering their shape, size and distribution. This temperature dependent changes can be used to tune the LSPR band for its application in optical sensing, where shifts in the position of the plasmonic band can be used to detect the presence of molecules. In this work, monometallic and bimetallic thin films were produced, using Au and Au+Ag as the noble metals, by reactive DC magnetron sputtering. To study the effect of composition, and morphologic changes promoted by the heat treatment in the LSPR peak, transmission electronic microscopy was used. Optical transmittance spectra were also measured, emphasizing in correlation of the LSPR band properties and the morphological characterization. Morphological and chemical analysis showed the crystallization of nanoparticles to temperatures above 300 ºC, with the mapping of bimetallic nanoparticles in Au+Ag plasmonic thin films. LSPR measurements revealed a different absorption band, with a blue-shift in the bimetallic films compared to the Au-TiO_2 films.

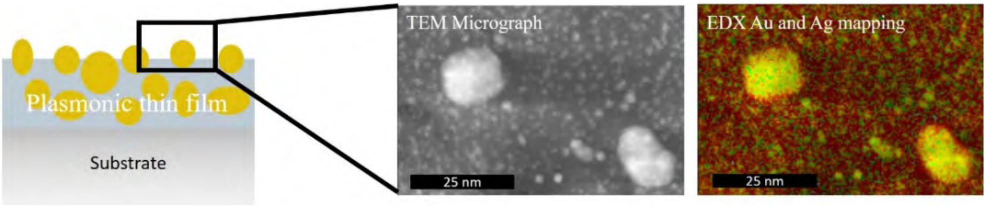

Figure 1. Nanoparticle analysis by EDX in Transmission electron microscopy

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PDMS degradation monitored by the LSPR response of an embedded AuNPs array

Tomáš Lednický[1], Tomáš Plichta[1,2], Zdenka Fohlerová[1], Attila Bonyár[3]*

[1]CEITEC – Central European Institute of Technology, Brno University of Technology, Brno, Czech Republic
[2]Institute of Materials Chemistry, Faculty of Chemistry, Brno University of Technology, Brno, Czech Republic
[3]Department of Electronics Technology, Budapest University of Technology and Economics, Budapest, Hungary
*E-mail: lednicky@vutbr.cz

Keywords: PDMS, degradation, X-ray, AuNPs

Polydimethylsiloxane (PDMS) has excellent properties such as a good optical transparency in the visible region, high flexibility and exceptional chemical stability, which made it a first choice material for fabrication and prototyping of microfluidic chips. Additionally, it is widely used in soft lithography or even medicine and cosmetics. Therefore, a study of its properties with respect to degradation and material modification holds a valuable significance for these fields.

In this work, we monitor the degradation of the top layer of a PDMS nanocomposite due to ionizing X-ray irradiation. This degradation is characterized by change of surface elasticity and chemical composition, which were monitored by a nanoindener system and XPS, respectively. Our findings correlate with similar works using UV light [1], gallium ions (keV) [2], or even protons (MeV) [3].

In addition, the phenomenon of localized surface plasmon resonance (LSPR) on embedded AuNPs array (particle diameter of 80 nm and 100 nm spacing) [4] is effectively utilized to measure changes in the PDMS matrix .

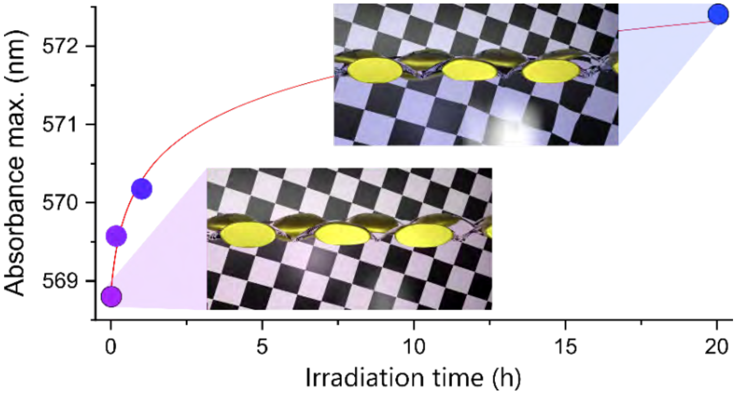

Figure 1. Illustration of the absorbance maxima for various X-ray irradiation periods of an embedded AuNPs array on top of PDMS matrix.

Acknowledgments

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Effect of the (geometrical) parameters of gold/silver nanoisland arrangements on their SERS properties

Petra Pál[1*], *László Balázs*[1], *Miklós Veres*[2], *László Himics*[2], *Attila Bonyár*[3], *Laura Juhász*[4], *István Csarnovics*[1]

[1]Department of Experimental Physics, University of Debrecen, Debrecen, Hungary
[2]Institute of Solid State Physics and Optics, Wigner RCP, Budapest, Hungary
[3]Department of Electronics Technology, Budapest University of Technology and Economics, Budapest, Hungary
[4]Department of Solid State Physics, University of Debrecen
[*]E-mail: p.petruka@gmail.com

Keywords: gold and silver nanoislands, surface-enhanced Raman scattering, plasmonics, photonic devices, sensors

In this work, the process of surface-enhanced Raman scattering (SERS) was studied on gold and silver nanoisland arrangements. Systematic investigations were carried out on different gold and silver nanoisland samples to determine how SERS enhancement depends on the morphology (particle size, interparticular distance) and optical parameters (plasmon wavelength) of the nanostructures. For this purpose, the metallic nanostructures were created by annealing thin film layers of gold and silver deposited by vacuum thermal evaporation onto glass substrates. The heat treatment (solid-state dewetting) took place at different temperatures (400 °C, 450 °C, 500 °C, and 550 °C) for different time periods (15, 30, 60 and 120 minutes), resulting in a variety of geometrical parameters (e.g. particle diameter, interparticle distance). The parameters of the created nanoislands, such as equivalent particle diameter, interparticular distance, and plasmon wavelength on the SERS enhancement efficiency were studied. The SERS capabilities of the samples were evaluated by measuring an analyte solution of benzophenone with three different excitation laser wavelengths. Scanning electron microscopy was used to measure the average particle diameter and average interparticle distance in order to correlate them with the obtained SERS enhancements. The influence of the geometric parameters of metallic nanoparticles and the laser wavelength on the surface-enhanced Raman process was evaluated.

By comparing the results obtained on the gold and silver nanoisland arrangements we can draw the following conclusions: Maximum SERS EF was obtained using 532 nm excitation source for gold and 488 nm laser irradiation for silver samples. This demonstrates the importance of the relationship between the excitation wavelength and the surface plasmon absorption properties and should be taken into account.

SERS EF showed a positive linear correlation with nanoparticle size and a negative exponential relationship with interparticle distance for both types of nanomaterials. This is due to the higher scattering efficiency (larger particle size) and the higher density of near-field hot spots on tightly packed particles.

Acknowledgments

This work was financially supported by the grant GINOP-2.3.2-15-2016-00041. The projects are co-financed by the European Union and the European Regional Development Fund. This work was supported by the VEKOP-2.3.2-16-2016-00011 grant, which is co-financed by the European Union and European Social Fund.

A new method to prepare sharp Tungsten tip for STM

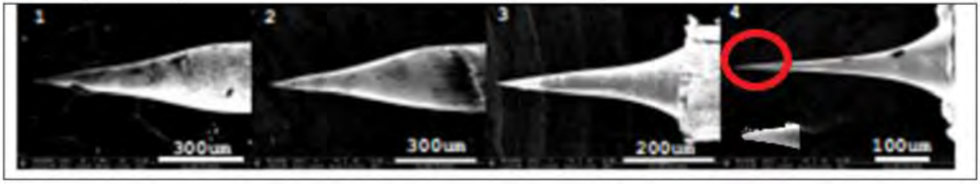
Saravanan. M. P[1], Ajay Verma[2], Ajay Gupta[3]*

[1]UGC DAE CSR, University Campus, Indore, India
[2]Institute of Engineering and Technology, DAVV, Indore, India
[3]Amity Center for Spintronic Materials, Amity University, Noida, India
[*]E-mail: ervanan@gmail.com

Keywords: tunnelling, STS, STM, etching, tungsten, current limiting, tip profile

From the time of invention of Scanning Tunnelling Microscope (STM) by Binning et al, monotonic advancement is observed in STM, Scanning Tunnelling Spectroscopy (STS) and equally in the field of tunnelling tip preparation. As the tip is one of the most crucial components of a STM in determining the resolution of the image obtained, various methods have been discovered and followed [1,2]. In this article a new approach of limiting the etching current is chosen to produce sharp tips whose tip size and radius of curvature (ROC) can be predetermined.

While Sodium Nitrate ($NaNO_3$) is used as electrolyte, Tungsten whose tip has to be made is made as an electrode and Platinum is used as the other electrode. An alternating voltage of 30 V is applied between the electrodes through a current limiting resister. Most of the literatures describes about the current cut off method to stop the etching process so as to keep the tip atomically sharp. In this current limiting method, the series resistor limits the maximum allowable current, hence the etching process is controlled which leads to have the tip profile controllable and attained tips in the order of 30 nm with 1Kohm resistor. This determines the cone angle and the ROC of the tips to be produced. The experimental set up is automated with a Keithley Source Measure Unit to measure the voltage across the resistor with respect to time and the current is calculated. The data acquisition is made with GPIB interface and LabVIEW. The following images explain the size of the tips produced with various current limiting resistors. By this simple and cost-effective method suitable tips can be prepared with precise tip size and ROC as per the required measurement without the usage of complex cut off circuits.



The SEM image shows the etched tips with higher limiting current to lower limiting current keeping the voltage same. (1) 10ohm, (2) 300 Ohm, (3) 800 Ohm, (4) 1000 Ohm,

Acknowledgments

Authors acknowledge Dr.R.Venkatesh and Dr.Satish Potdar , UGC DAE CSR, Indore for SEM measurements of the etched tunnelling tips.

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T2: Biointerfaces

Interaction of the thin bioactive ceramic coating on the bioinert Si_3N_4 implant

Katalin Balázsi[1], Tamás Zagyva[1], Riku Lovics[1], Tibor Sopcak[2], Csaba Balázsi[1]*

[1]Thin Film Physics Department, Institute for Technical Physics and Materials Science,
Centre for Energy Research, Budapest, Hungary
[2]Institute of Material Research, Slovak Academy of Sciences, Kosice, Slovakia
[*]E-mail: Balazsi.katalin@energia.mta.hu

Keywords: bioceramic, silicon nitride, interface, electrospraying

Silicon nitride has recently been introduced as a commercially available bioceramic for total hip replacements with outstanding mechanical properties. The aim of this study was to produce homogeneous hydroxyapatite/polyethylene glycol (HA/PEG) composite coating on carbon nanotube (Si_3N_4/MWCNT) or graphene reinforced silicon nitride (Si_3N_4/graphene) substrate by electrospray deposition method. The separation of HA and PEG particles during the deposition process could be avoided successfully by using lower flow rate and voltage parameters. The HA/PEG composite showed significantly better mechanical properties (e.g. cohesion strength, scratch resistance) than the pure HA layer. The bioactive/bioinert interface has influence on the final biological, tribological or mechanical properties.

Electrosprayed coating with the optimized surface´s properties of HA bioceramic thin coating could be a good alternative for accelerating the osseointegration process on the surface of the implants.

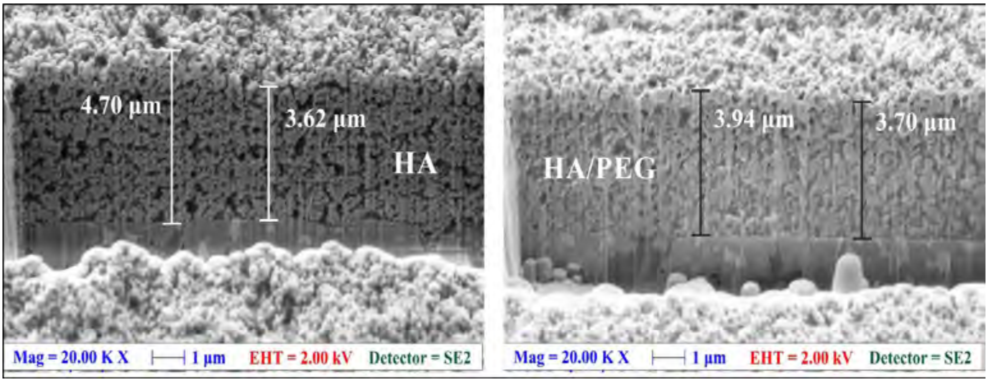

Figure 1. SEM image of HA coated Si_3N_4 implant.

Acknowledgments
Authors would like to thank to Levente Illés (EK MFA) for SEM measurements.

In situ spectroscopic ellipsometry studies of membrane affinity of biodegradable polylactide-co-glycolide (PLGA) nanoparticle systems

Alekszej Romanenko[1,2], Emil Agócs[1], Éva Kiss[3], Peter Petrik[1], Gergő Gyulai[3]*

[1]Centre for Energy Research, Konkoly Thege Miklós út 29-33, H-1121 Budapest, Hungary
[2]Doctoral School of Chemistry, Roland Eötvös University, Pázmány Péter sétány 1/A, H-1117 Budapest, Hungary
[3]Roland Eötvös University, Pázmány Péter sétány 1/A, H-1117 Budapest, Hungary
[*]E-mail: alekszej@list.ru

Intensive research over the past decades has led to the development of new delivery systems to enhance the therapeutic efficacy of drugs [1]. These carrier systems allow controlled, targeted delivery with lower doses and fewer side effects. Biodegradable polyester-type polymers, polylactide-co-glycolides (PLGA), are of particular importance because of their ability to be absorbed and metabolized by the body. PLGA nanoparticulate systems can be easily made using the nanoprecipitation method [2]. The surface properties of PLGA nanoparticles play a crucial role in their colloidal stability and interaction with the cell membrane, therefore in the therapeutic applicability of these nanosuspensions [3]. Several types of PLGA nanoparticles were prepared with various surface coatings and modifications. Their sizes and morphologies were determined by atomic force microscopy (AFM) and dynamic light scattering, while surface charge was investigated by zeta potential measurements. Interactions with lipids, the major components of the cell membrane, were investigated by *in situ* spectroscopic ellipsometry. The lipid bilayers have been used as model membranes on the surface of silicon. The adsorption isotherms and kinetics of nanoparticles were also investigated at different pH and ionic strength media. Changes in morphology of the solid-liquid interfaces were examined as well by the AFM. The results obtained could facilitate the rational design of drug carrier nanoparticle systems with regulated membrane affinity.

Acknowledgement

These studies were supported by grant (VEKOP-2.3.3-15-2017-00020) from the European Union and the State of Hungary, co-financed by the European Regional Development Fund and the National Research, Development and Innovation Fund of Hungary (reference numbers: NVKP 16-1-2016-0014 and OTKA K131515). This work was completed in the ELTE Institutional Excellence Program (1783-3/2018/FEKUTSTRAT) supported by the Hungarian Ministry of Human Capacities.)

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T3: Plasma Science & Technique

Investigating the effect of plasma activation's hydrophobic recovery on cell adhesion and viability

Laura Astoreca[1,2], Pieter Cools[1], Mahtab Asadian[1], Sheida Aliakbarshirazi[1], David Schaubroeck[2], Rino Morent[1], Herbert De Smet[2], Nathalie De Geyter[1]*

[1]Research Unit Plasma Technology (RUPT), Ghent University, Department of Applied Physics, Faculty of Engineering and Architecture, Sint-Pietersnieuwstraat 41, 9000 Ghent, Belgium
[2]Center for Microsystems Technology (CMST), Ghent University and imec, Technologiepark 126, B-9052 Ghent, Belgium
[*]E-mail: Laura.Astorecaalvarez@ugent.be

Keywords: polyimide, surface modification, plasma activation, biocompatibility, fibroblasts

BPDA-PPD polyimide (PI) is commonly used in the packaging of implantable medical devices as it has relatively good water barrier properties and is biocompatible. Its biocompatibility can be further improved by plasma surface modification to ensure a successful integration of the device with the surrounding tissue. PI films were subjected to air and N_2 plasma activation, studying the cell-surface interactions via *in vitro* MTT and live/dead cell tests with human foreskin fibroblasts 1 and 7 days after cell seeding. Three conditions for the activation of the PI were studied: (1) fully saturated surface with functional groups, (2) fully saturated surface with functional groups and subjected to 24 hours of hydrophobic recovery and (3) non-saturated surface with the same hydrophilicity as the films subjected to hydrophobic recovery as in (2). A loss of hydrophilicity occurred after the 24 hours for air and N_2 activations, and small variations in the concentration of O-functionalities were observed by XPS. Meaning that the functional groups introduced by the activation reoriented/migrated towards the bulk of the films and, though not available at the surface, were still present on the subsurface. All the activated films presented better cell-surface interactions than the untreated PI. The saturated films subjected to hydrophobic recovery (2) presented lower initial cell adhesion 1 day after seeding, but as good or even higher cell proliferation after 7 days than the saturated films not subjected to hydrophobic recovery (1). Thus, the functionalities from the subsurface were progressively available at the surface when immersed in the culture media, reversing the hydrophobic recovery effects. The non-saturated air activation (3) led to poor cell-surface interactions as the exposure time was so short that the treatments were not stable, barely incorporating O-functionalities. The non-saturated N_2 activation (3) incorporated almost the same amount of O-functionalities as the N_2 saturated activations (1,2), which together with the moderate hydrophilicity of the films led to better cell-surface interactions. The effect of the hydrophobic recovery on the cell-surface interactions was minimal. It lowered the initial cell adhesion but was progressively reverted as the samples were immersed in the culture media achieving comparable results of cell proliferation. The availability of functionalities was more determining than a moderate hydrophilic surface for the cell-surface interactions.

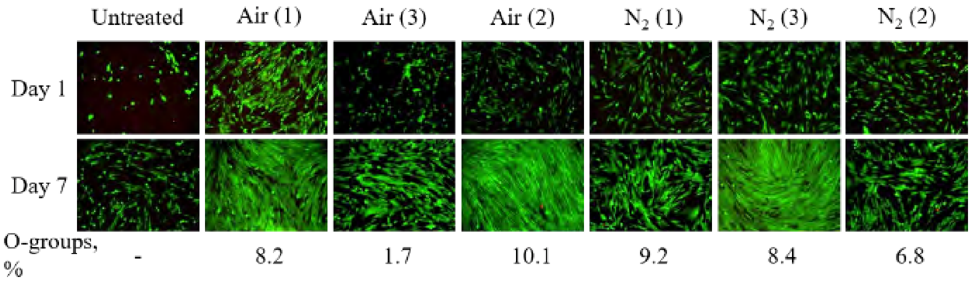

Figure 1. Concentration of O-functionalities on the surface and live/dead fluorescent images (4x magnification) of untreated and plasma activated PI 1 and 7 days after cell seeding. Green and red represent live or dead cells respectively.

Acknowledgments

This research was supported by a grant from the Research Foundation Flanders (G.0867.17N).

Spectroscopic analysis of MoS_2 thin layer using simultaneous vacuum UV and broadband UV-NIR Laser-Induced Breakdown Spectroscopy

Vishal Dwivedi[1]*, Alicia Marín Roldán*[1]*, Matej Veis*[1]*, Michal Bodík*[2]*, Peter Šiffalovič*[2]*,*
Eva Majková[2]*, Pavel Veis*[1*]

[1]Department of Experimental Physics, Faculty of Mathematics, Physics and Informatics, Comenius University, Mlynská dolina F2, 842 48 Bratislava, Slovakia
[2]Institute of Physics, Slovak Academy of Sciences, Dúbravská cesta 9, 845 11 Bratislava, Slovak Republic
[*]E-mail: pavel.veis@fmph.uniba.sk

Keywords: LIBS, MoS_2, vacuum UV

The present work relates to the qualitative study of the constituent elements of MoS_2 thin layer deposited on the surface of Si, Al, and Cu substrate respectively, using Laser-Induced Breakdown Spectroscopy (LIBS). The MoS_2 was prepared using standard liquid exfoliation method and deposited on the substrate using modified Langmuir Schaefer method [1-3]. High fluence Q-switched Nd:YAG laser has been used as a source to create plasma on the surface of the sample. Emission from the plasma has been collected using fiber and fed to two spectrometers simultaneously: broadband UV-NIR echelle type spectrometer (230 nm–950 nm, ME 5000, Andor) and VUV (114–295 nm, McPherson), both equipped with iCCD camera (iStar, Andor) [4]. Measurements were performed inside the vacuum chamber at the low pressure inert gas atmosphere. Spectral lines were identified in the spectra by using the NIST database. We observed spectral lines of S (S I: 142 nm–45 nm; 147 nm–149 nm; 180–183 nm, S II: 125 nm–126 nm, S III: 11–120 nm) from three degrees of ionization, allowing us to determine electron temperature in the early stage of the plasma plume [5]. Saha-Boltzmann plot has been used for the determination of electron temperature, while electron density has been evaluated using the stark broadening of H-alpha line at 656.3 nm. This preliminary work can be useful for future quantitative analysis of this kind of the samples. Results are encouraging and will be presented in detail during the ICTS-JVC-2020.

Acknowledgments

This work has been supported by SRDA (No. APVV-15-0641, and No. APVV-16-0612) and Scientific Grant Agency of the Slovak Republic (VEGA No. 1/0903/17). VD would like to thank the Comenius University for the UK Young Grants (UK/64/2020_FMFI).

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T4: Surface Engineering

Comparison of applied properties of selected hard coatings deposited in different industrial coating units

Miha Čekada[*]*, Peter Panjan, Matej Drobnič, Aljaž Drnovšek*

Department of Thin Films and Surfaces, Jožef Stefan Institute, Ljubljana, Slovenia
[*]E-mail: miha.cekada@ijs.si

Keywords: hard coating, PVD, magnetron sputtering, cathodic arc evaporation

Standard hard coatings have well-known mechanical, physical and chemical properties; this includes also knowledge on the dependence of these properties on deposition parameters, say bias voltage. Such experiments can be relatively easily reproduced in a lab environment; however, in an industrial environment there are several other influences which should be taken into account. Foremost, substrate mounting plays a major role (number of rotation axes), to be accompanied by the chamber design and finally the local environment of the batch the sample was put into.

In this work we deposited several types of commercially applicable hard coatings: single-layer (TiN, CrN and TiAlN), double-layer (TiAlN+DLC), multilayer (TiAlN/TiN and AlTiN/TiN) and nanocomposite (TiAlSiN). Three different deposition techniques were used: magnetron sputtering, cathodic arc evaporation and thermionic arc evaporation. Identical D2 tool steel substrates were used in all the cases, which were mounted in three different rotation modes. To evaluate reproducibility three samples were put in each configuration. All the samples were then evaluated regarding basic properties such as thickness, chemical composition, and topography, where a special emphasis was put on the growth defect density. Consequently mechanical properties were measured including hardness, Young's modulus and adhesion (by scratch test).

The results show that the sample mounting (i.e. number of rotation axes) often appears to be the most prominent factor of influence, primarily by influencing the coating thickness and microstructure. For instance, a single-layer TiAlN and a nanolayer TiAlN/TiN, both mounted at double rotation, have a more similar hardness than either coating mounted at single rotation. The influence of the deposition method comes in a third place. The main summary of this study is to provide a systematic overview of samples, deposited and evaluated in an identical way.

Functionalization of microfluidic devices by microstructures created by proton beam lithography

Emad Nady[1*], *Gyula Nagy*[2], *Róbert Huszánk*[2]

[1]University of Debrecen, Debrecen, Hungary
[2]Institute for Nuclear Research, Debrecen, Hungary
[*]E-mail: emad.nady@atomki.mta.hu

Keywords: proton beam writing, microfluidics, microfluidic passive mixers

Microfluidic devices have become important part of technology nowadays in numerous fields of application, such as chemical reactions, biosensors, synthesis of nanomaterials, diagnostic device for detection of biological samples, etc. Thanks to their small dimensions, their surface to volume ratio is extremely high. Because of this, they offer unique physical characteristics, very different ones from the macroscopic world. At the same time, the Reynolds number of the fluid flow in them are typically below 1, so laminar flow dominates. This makes the mixing of two different fluid particularly difficult, and occurs only by diffusion. Therefore, the mixing is still a great challenge for researchers working with microfluidic devices. Due to this, one of their important field of research and development is mixing at microscale. Micromixer is a device which is used to mix two or more fluids in a micro scale channel to handle micro and nanoliter volume of fluids.

Generally, micro devices are created by UV-lithography using SU-8 master, moulding with poly (dimethyl-siloxane) (PDMS) silicone polymer, which is then polymerized. The PDMS surfaces of the two parts of the microfluidic system are bonded by air plasma treatment after alignment.

As a new fabrication approach, PDMS microstructures were integrated into PDMS micro-devices by combining proton beam lithography (direct writing technique utilizing focused, few MeV proton beams, to create micro- and nanoscale structures) and conventional UV lithography fabrication techniques. This way, the microstructures and the micro-devices can be made from the same material, which is not only useful, but in case of certain applications, it is essential (e.g. cell separation, etc.).

This work deals with the design of various microfluidic devices with and without integrated microstructures. The investigation involves the computer simulation and optimization, and the fabrication with the above mentioned methods. Finally, the analysis of the mixing efficiency of the micromixer devices was realized with UV/vis spectroscopy at different fluid flow rates. Compared to the small size of the whole mixing chip, very high mixing efficiency could be achieved.

Influence of the static mixing with high energy ions for an interface between BN film and TiN substrate on the compositional and topographical evolution of the surface

Toshiro Kobayashi[1], Reza Valizadeh[2], Matthew Lambrinos[3], Masaya Takeuchi[4], Akinobu Yamaguchi[4], Uichi Utsumi[4]*

[1]Dept. of Electronics & Control Engineering, National Institute of Technology, Tsuyama College, Okayama, Japan
[2]Science and Technology Facilities Council (STFC/DL/ASTeC) Daresbury, Laboratory Accelerator Science and Technology Centre, Daresbury, UK
[3]FAI PATENTS, Palo Alto, USA
[4]Laboratory of Advanced Science and Technology for Industry, University of Hyogo, Hyogo, Japan
*E-mail: t-koba@tsuyama-ct.ac.jp

Keywords: interface mixing, ion implantation, boron nitride, titanium nitride

The creation of a mixed layer was studied: Ar, N and Ti ions having energy from 70 to 80 keV were implanted into an interface between a BN film and TiN under layer, and influence of ion implantation condition on the compositional and topographical evolution on the surface was investigated, and following results were obtained.

(a) 80keV Ar^+ ion implantation to a BN (650Å)/TiN under layer:

While a sample as deposited was cracked after a scratch test, a sample implanted with Ar ions at a fluence of 5×10^{15} ions/cm^2 did not change, indicating the improvement of brittleness or adhesion of the BN layer. At higher Ar ion fluences greater than 5×10^{16} ions/cm^2, the BN layers were removed as powder-like aspect. By SEM observation, it was found that blisters formed at ion fluences greater than 5×10^{16} ions/cm^2.

(b) 70keV Ti^+ ion implantation to a BN (650Å)/TiN under layer:

It is found that after the scratch test no crack and delamination was observed at a 70keV Ti^+ ion fluence of 5×10^{15} ions/cm^2 and at ion fluences greater than $1x10^{17}$ ions/cm^2 , whereas at an ion fluence of 5×10^{16} ions/cm^2 crack and delamination were observed. It is suggested that the reason for the crack is not due to the formation of bubbles but due to embrittlement of the film or interface. The reason for no cracking at high ion fluences is suggested that the original BN film and the TiN under layer are altered properly into a Ti-B-N graded layer by both the mixing effect of Ti^+ irradiation and the implanted Ti atoms. Consequently it is suggested that Ti ion implantation to BN films on TiN substrate is one of the effective methods so that a compositionally graded layer consisting of Ti, B and N is produced.

High temperature tribological behavior of TiAlN and nanolayer TiAlN/TiSiN coatings deposited on various tool materials

Vladimir Terek[1*], *Lazar Kovačević*[1], *Aleksandar Miletić*[1 2], *Branko Škorić*[1], *Aljaž Drnovšek*[3], *Peter Panjan*[3], *Pal Terek*[1]

[1]University of Novi Sad, Faculty of Technical Sciences, Trg Dositeja Obradovića 6, Novi Sad, 21000, Serbia
[2]Polytechnique Montreal, Department of Engineering Physics, Montreal, Quebec H3T 1J4, Canada
[3]Jožef Stefan Institute, Jamova 39, Ljubljana, 1000, Slovenia
[*]E-mail: vladimirterek@uns.ac.rs

Keywords: PVD coatings, TiAlN, TiAlSiN, tribology, high temperature, substrate material

Evaluations of novel coatings for protection of tools used for high temperature processing of materials are mostly concentrated on evaluation of their microstructure, mechanical properties and oxidation resistance. Much less effort is given to investigation of their tribological behavior, especially at elevated temperatures. Additionally, in a lot of investigations concerning the high temperature tribological behavior of coatings, the effect of substrate material on test results is frequently overlooked. Therefore, this investigation aims to contribute to better understanding of results obtained in high temperature tribological tests of hard coatings, which were deposited on different kinds of tool materials. In this investigation, standard TiAlN coating was prepared by cathodic arc deposition and a novel nanolayer TiAlN/TiSiN coating was prepared by unbalanced magnetron sputtering system. Disc samples made of hot-working tool steel (EN X38CrMoV5), were coated with both kinds of coatings, while plasma nitrided X38CrMoV5 steel and cemented carbide (WC/Co) samples were coated with TiAlN/TiSiN coating. Coatings mechanical properties were evaluated by nanoindentation. Tribological behavior of coatings at room temperature, 500, 600, 700 and 760 °C in air and N_2 ambient, were tested against Al_2O_3 ball using high temperature pin-on-disk tribometer. After the tests, wear tracks were evaluated by stylus profilometry, confocal microscopy (CFM) and focused ion beam (FIB), equipped with energy dispersive spectroscopy (EDS). Hardness of TiAlN coating was $3050HV_{0.05}$ while hardness of TiAlN/TiSiN coating was $2780HV_{0.05}$. At room temperature (RT) the steady state coefficient of friction (COF) of TiAlN was 0.75 and of TiAlN/TiSiN coating was 0.85. In test at 500 °C, TiAlN coating was not completely worn off and it displayed higher coefficient of friction (COF) and lower wear rate than in RT tests. It was revealed that TiAlN coating tested at 600 and 700 °C suffered from cracking and oxidation of the underlaying substrate. Formation of Fe–O in wear tracks caused positive material wear which consequently decreased the monitored coating wear. Such behavior is also found for TiAlN/TiSiN coating deposited on X38CrMoV5 steel. In all cases where substrate tribo-oxidation occurred, at some point in the tests the value of COF decreased to values lower than one recorded in RT tests. Such behavior may be the consequence of sliding against Fe–O layer. In case of TiAlN/TiSiN coating, substrate material oxidation was for nitrided steel and cemented carbide substrates detected at 700 and 760 °C respectively. However, in N_2 ambient the TiAlN/TiSiN coating survived even at 760 °C. For TiAlN/TiSiN coating in both ambientes, the average values of COF (~0.85) did not significantly vary on testing temperature, but the coating wear increased with increase in temperature.

Acknowledgments

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T5: Surface Science

Grain boundary diffusion in thin Cu/Si//Si systems

Eszter Bodnár[*], *Viktor Takáts, Tamás Fodor, Kálmán Vad*

Institute for Nuclear Research, Debrecen, Hungary
[*]E-mail: bodnar.eszter@atomki.mta.hu

Keywords: Grain-boundary diffusion, thin film, CuSi, low energy ion spectroscopy, scanning tunnelling microscopy

Silicon diffusion from an amorphous Si layer through grain boundaries (GB) of a polycrystalline Cu film was studied in the temperature range of 130-150 °C. The thickness of the Cu film was 40 nm. The Si amorphous layer (80 nm) and polycrystalline Cu layer were successively deposited at room temperature onto a Si (111) wafer by magnetron sputtering. Appearing time of Si atoms diffused through the copper layer was detected on the surface by Low Energy Ion Scattering (LEIS) spectroscopy with high sensitivity. Grain boundary diffusion coefficient could easily be calculated from this appearing time since the root-mean-squared displacement of large number of diffusant atoms in grain boundaries can be written by the well-known Einstein-Smoluchowski relation, i.e. by $\sqrt{\langle r^2 \rangle} = \sqrt{6Dt}$, where $\langle r \rangle$ is the mean displacement, D is the coefficient of diffusion, t is the time. In our case the mean displacement corresponds to the film thickness h. In the experiments we studied not only the temperature dependence of diffusion coefficient, but its dependence on the Cu film thickness, as well.

Ellipsometric porosimetry investigation of mesoporous silica sol-gel coatings

Lenke Kócs[1], Emőke Albert[1], Bálint Fodor[2], Péter Basa[2], Csaba Major[3], András Szalai[3], György Sáfrán[4], Zoltán Hórvölgyi[1,]*

[1]Department of Physical Chemistry and Materials Science, Centre for Colloid Chemistry, Faculty of Chemical Technology and Biotechnology, Budapest University of Technology and Economics, H-1521 Budapest, Hungary
[2]Semilab Semiconductor Physics Laboratory Co. Ltd, H-1117 Budapest, Hungary
[3]Hungaro Lux Light Ltd., H-1171 Budapest, Hungary
[4]Institute of Technical Physics and Materials Science, Centre for Energy Research, H-1121 Budapest, Hungary
[*]E-mail: zhorvolgyi@mail.bme.hu

Keywords: mesoporous, silica coatings, ammonia treatment, double-layer formation, ellipsometric porosimetry, porosity, pore size distribution

Mesoporous silica layers were prepared by sol-gel deposition technique (dip-coating) on various substrates (silicon, polycarbonate, microscope glass and quartz). Mesopores were formed by the soft templating method using Pluronic PE10500 triblock copolymer. To stabilize the coating, the freshly deposited layers were aging in the atmosphere of aqueous ammonia solution. Two types of thermal curing were implemented depending on the substrates: a low-temperature heat treatment at 120°C for 13 hours, and high-temperature heat treatment at 480°C for 1 hour. The heat treatments were followed by leaching of the copolymer molecules or the water-soluble by-products.

TEM investigations revealed a very thin layer with mesoporous structure (face centred cubic, fcc). UV-Vis spectroscopy measurements gave evidence of a significantly improved and very long-lasting light transmittance of the layers on the transparent substrates, which confirms our previous results [1].

The ellipsometry and ellipsometric porosimetric (EP) [2] studies in the present work revealed a special “two-layer” structure of coatings. The applied synthesis techniques promoted the formation of a double layer structure with distinct porosity and pore size distributions. An ellipsometric model has been developed that can describe this bilayer structure. This optical model was used to determine the porosity, mean pore size and pore size distribution according to the modified Kelvin equation applied to the adsorbed and desorbed solvent quantities. We also investigated the sensitivity and robustness of these ellipsometric models. Independent, Effective Medium Approximation models fitted on the ellipsometric measurements correlate with the EP results. The results indicate a low porosity (20–30%) upper layer and a high porosity (70–80%) lower layer.

According to the experimental results, the unique structural change is due to the ammonia treatment, which is responsible not only for the significant increase in pore sizes but also for the considerable difference in the porosity of the outer and inner layers. The experimental results showed that the special structural rearrangement did not depend on the substrate types and the different circumstances of the preparation (e.g. rate of deposition) which also confirmed that the structural rearrangements took place during the ammonia treatment. The preparation conditions can only influence the relative thickness of the upper (outer) and the lower (inner) layer in the investigated samples. The denser outer layer protects the coatings from harmful environmental effects and ensures a long-lasting optical stability.

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Focusing on sub-processes timing in the formation kinetic of droplet-epitaxially grown III-V-based quantum dot

Ákos Nemcsics[*]*, Zoltán Farkas, Antal Ürmös*

Institute of Microelectronic and Technology, Obuda University, Budapest, Hungary
[*]E-mail: nemcsics.akos@kvk.uni-obuda.hu

Keywords: droplet-epitaxy, GaAs, quantum dot, size distribution

Currently both the growth technology and the growth kinetics of self-assembled quantum structures are studied intensively. The research aims to understand basic physical processes and to explore utilization possibilities. Size, shape and surface distribution of quantum dots are crucial regarding the utilization.

In recent paper, we investigated droplet epitaxially grown GaAs quantum dots on AlGaAs surface. Our study focused on the ranking preference of quantum dots evolution processes. The growth experiments were performed in a solid source molecular beam epitaxy system. The sample was quenched immediately after the crystallization phase and measured with atomic-force-microscopy technique. Quantum dots with various volumes were produced by fast crystallization without annealing. Thus, a frozen phase of the growth process was obtained. The quantum dots of different sizes were considered as snapshots of a single growth process as technology was identical. The height and lateral sizes were studied as functions of the volume.

We found that, during the quantum dot evolution, the most preferred process was the orientation dependent elongation. The second preferred one was the endeavor for minimal base perimeter. The least preferred process directed to the formation of the symmetrical side facets.

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T6: Thin film growth mechanism and models, new approaches

Fine gas inlet regulation down to base pressure of a sputtering system by means of a peristaltic pump

György Sáfrán, Noémi Szász, Gergely Dobrik, Miklós Serényi*

Institute for Technical Physics and Materials Science, Centre for Energy Research, Budapest, Hungary
*E-mail: safran.gyorgy@energia.mta.hu

Keywords: fine gas inlet regulation, peristaltic pump, concentration spread thin film, oxynitrides, RF sputtering

Our aim was the synthesis of concentration spread samples in order to reveal the refractive index and extinction coefficient of RF sputtered Si- and Hf- oxynitride films in a wide range of composition. According to the „one sample concept" micro-combinatorial technique [1] the 25x10 mm^2 Ge substrate was moved below a shutter with a narrow slot during film deposition meanwhile the ratio of partial pressures of reactive gases P_{O2}/P_{N2} have been, monotonously, decreased. However, we faced two problems to implement a variable inlet of O_2 (1) the commercially available gas flow regulators do not provide and regulate small flow rates below a few tens of 1 sccm and (2) we wanted to take advantage of a simple, self-regulating gas inlet. As a solution a small capacity (1 sccm, at max) peristaltic pump connected to a small-volume container, variable up to 100 cm^3, was applied for gas inlet. The pump was driven at a constant speed to deliver 1 cm^3/min volume of oxygen. The constant volume transport resulted in a gradual decrease of the pressure in the container, therefore a decrease of the amount (mass/min) of the delivered gas from an initial value determined by the volume and/or pressure of the container. The partial pressures of argon and nitrogen were kept constant at 0.2 and 1.8 Pa, respectively.

Figure 1 shows the experiment setup (on the left) and the O_2 partial pressure change in the vacuum chamber during oxygen inlet delivered by the peristaltic pump (on the right).

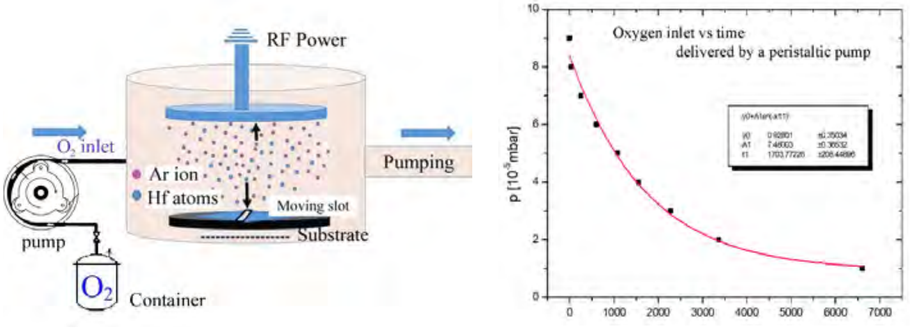

Figure 1. RF sputter deposition of concentration spread oxy-nitride samples prepared for optical measurements and (in the left)and time dependent partial pressure in the chamber due to oxygen inlet from a 48 cm^3 vessel delivered by a peristaltic pump; inset shows the fitting parameters of the function (in the right).

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One sample concept µ-combinatory for assemblage of databases of binary films by TEM, EDS, RBS, ellipsometry and nano-indentation

G. Sáfrán[1 *], *P. Petrik*[1], *B. Kalas*[1], *M. Fried*[1], *Zs Zolnai*[1], *T. Lohner*[1], *N. Szász*[1], *N.Q. Chinh*[1], *J. Gubicza*[1], *N. Hegedüs*[2,3], *M. Serényi*[1]

[1]Institute of Technical Physics and Materials Science, Research Centre for Natural Sciences, Budapest, Hungary
[2]Roland Eötvös University, Budapest, Hungary
[3]Óbuda University, Doctoral School on Materials Sciences and Technologies, Budapest, Hungary
*E-mail: safran.gyorgy@energia.mta.hu

Keywords: full range concentration gradient sample, high throughput synthesis and measurement

Binary phase diagrams are available for bulk materials, but, do not exist for thin films. For screening the composition dependent structural, physical and chemical properties of binary films, a high throughput method "one-sample concept micro-combinatory" has been worked out and patented [1, 2]. The particular feature is that a single concentration spread sample comprises the entire binary layer system hence we need to synthetize and measure only one sample that meets the requirements of the analytical technique: A sample for TEM is deposited onto a 3mm grid, with a concentration gradient of typically 0.1%/µm, while that for XRD, RBS, ellipsometry and nano-indentation onto a 12x25mm size Si substrate, with a gradient of 0.5 %/µm (Fig.1). The samples are deposited by dual DC or RF sputtering. The concentration spread is created so that a slot in a shutter is swept over the substrate, meanwhile, the deposition rates of the two sources, or the partial pressures of gases (O_2, N_2, Ar etc.) are regulated. The samples were measured by a 200kV C_s-corrected FEI Themis TEM equipped with EDS. The technologically important Al-Mg compound samples were measured by TEM and by nano-indentation using a Wickers diamond tip. Unexpectedly high hardness was revealed in films with 1–20 at% Mg, that together with TEM and AFM microstructural characterization allowed us to reveal the hardening mechanism upon Mg addition [3]. The results confirmed the modified Hall-Petch relationship. Complete materials libraries of the refractive index (n) and extinction coefficient (k), of a-Si-Ge:H, Si-O-N and Hf-O-N have been collected within a few hours by ellipsometry using a computer controlled positioning, measuring and data collecting system [4].

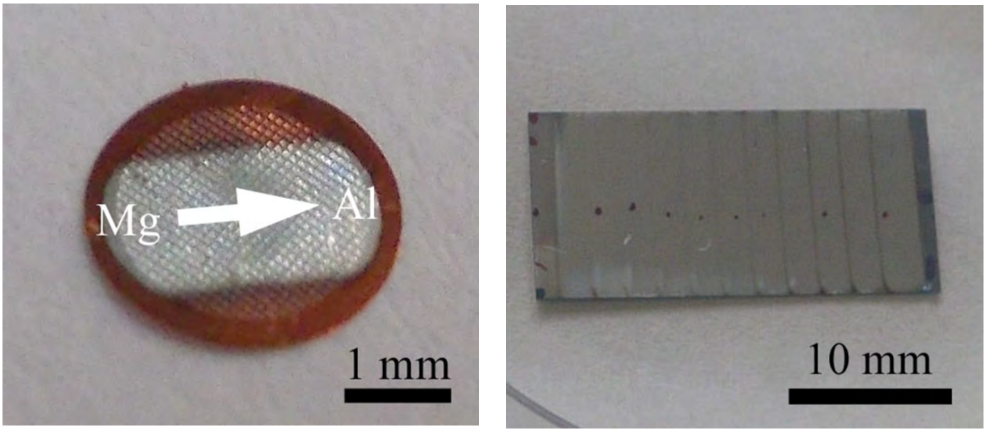

Figure 1. Mg-Al μ-combinatorial sample prepared for TEM (left) and for nano-indentation hardness test (right)

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Interpretation of hydrogen incorporation into amorphous silicon by reactive sputtering mechanism

Nikolett Hegedüs[1,2*], *Riku Lovics*[2], *Miklós Serényi*[2], *Péter Petrik*[2], *Katalin Balázsi*[2], *Csaba Balázsi*[2]

[1]Doctoral School on Materials Sciences and Technologies, Óbuda University, Budapest, Hungary
[2]Institute for Technical Physics and Materials Science, Centre for Energy Research, Budapest, Hungary
[*]E-mail: nhegedus@guardian.com

Keywords: amorphous silicon, radio frequency sputtering, hydrogenation, Berg modell

The electrical and structural properties of hydrogenated amorphous Si (a-Si) material are particularly affected by the hydrogen incorporated and its bonding configuration. On one hand, H is known to be very efficient in reducing the density of dangling bonds responsible for deep levels in the bandgap. The density of dangling bonds can be reduced by hydrogenation to a value, which is quite acceptable for device applications. On the other hand, the H bonding configuration may negatively affect the microstructure of the amorphous lattice. In the amorphous material hydrogen is bonded in two modes: as randomly distributed H bonded at isolated network sites (passivating the dangling bonds) and as H bonded in the form of clusters accommodated on the surfaces of voids.

Nano- and micro-voids have been detected in a-Si. Such voids are normally present in as-prepared amorphous materials and it is known that the voids are still one of the major defects in hydrogenated a-Si. Being empty spaces, they cause density reduction that can change the refractive index, electronic defect states and anomalous stress distribution.

This work is a contribution in the field of the H content in hydrogenated a-Si single layers deposited by radio frequency (RF) sputtering. It was prompted by the need to improve understanding of our previous results about the incorporation of H into Si layer measured by Elastic Recoil Detection Analysis (ERDA). The results of the calculation of Berg model of the reactive sputtering process reported here support and confirm our hypothesis that the mechanism of H incorporation can be considered as a reactive sputtering process. Our assumption was based on the fact that the amount of the incorporated hydrogen is proportional to the partial pressure of H and the plasma current similarly to the Berg model: hydrogenation may occur through ionization of molecular hydrogen followed by reactions between elemental target atoms to compound molecules. The results of our calculations can be used for the simulation of RF sputterd a-Si:H thin films by Berg modell. The low ionization rate for hydrogen in the sputtering system may limit the efficiency of hydrogenation of other silicon compounds like SiO_2 or Si_3N_4.

T7: Thin film multilayer and superlattices

Optical properties of very thin Ag films deposited on Al interlayer

Ryouto Atsuya, Takuya Hirano, Midori Kawamura, Takayuki Kiba, Yoshio Abe, Kyung Ho Kim*

Department of Materials Science and Engineering, Kitami Institute of Technology, Kitami, Japan
*E-mail: kawamumd@mail.kitami-it.ac.jp

Keywords: Ag film, interlayer, optical property, roughness

Due to its low emissivity (e), Ag thin film in thickness of around 10 nm is an essential constituent as Low-e coating for windows, and it contributes for energy-saving for the buildings. It is known that a thin film in such thickness is in transition state between continuous and discontinuous films. Therefore, it is important that usage of an appropriate interlayer and/or upper layer to show sufficient properties such as a high transmittance in visible region and reflectance in infrared region. It has been reported that interlayers, such as Si, Ge, and W, can be useful to form smooth very thin Ag films. We expect that Al is potential candidate because of the high bond dissociation energy of Ag-Al. In the present study, we investigate optical properties of very thin Ag films having interface and surface Al nanolayers.

We deposited Al interlayer (1 nm) and Ag films (6-15 nm) successively on glass substrates by vacuum evaporation method without breaking the vacuum. Then, sheet resistance, infrared reflectance, transmittance in visible region were investigated. Surface of some samples were observed using AFM. The sheet resistance of thinner films below 13 nm decreased considerably by the introducing the interlayer. In these samples, surface roughness was also smaller. Fig. 1 shows average transmittance of the samples and it is found that influence of the interlayer is significant at thinner Ag films. Fig. 2 shows reflectance of the samples. It is found that thinner Ag film shows almost the same reflectance with thicker (15 nm) film by the use of the interlayer. Therefore, higher optical properties obtained by introducing the interlayer were confirmed which also leads to reduction of the material cost. Moreover, an additional surface Al nanolayer on the structure is found to keep the high optical properties of Ag/Al films in Figs. 1 and 2. Because we confirmed a high environmental stability effect by the deposition of Al nanolayer previously[1)], very thin Ag film in the Al/Ag/Al structure can have the high stability, too.

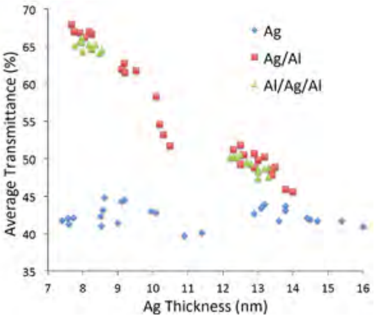

Figure 1. Average transmittance of the samples.
(l =380 nm – 780 nm)

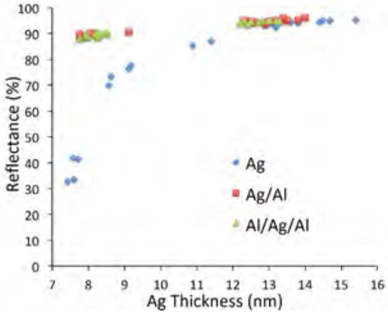

Figure 2. Reflectance of the samples
(l=10 mm)

Acknowledgments

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Ge quantum dot lattices in alumina prepared by nitrogen assisted deposition: structure and photoelectric conversion efficiency

Marija Tkalčević[1*], *Lovro Basioli*[1], *Iva Šarić*[2,3], *Jordi Sancho Parramon*[1], *Sigrid Bernstorff*[4], *Mladen Petravić*[2], *Maja Mičetić*[1]

[1]Ruđer Bošković Institute, Bijenička cesta 54, 10000 Zagreb, Croatia
[2]University of Rijeka, Radmile Matejčić 2, 51000 Rijeka, Croatia
[3]Center for Micro- and Nanosciences and Technologies, University of Rijeka, Radmile Matejcic 2, 51000 Rijeka, Croatia
[4]Elettra sincrotrone, S.C.p.A., Strada Statale 14 km 163,500 in AREA Science Park, Basovizza/Trieste 34149, Italy
[*]E-mail: Marija.Tkalcevic@irb.hr

Keywords: germanium QDs, multilayer deposition, multiple exciton generation

Thin films comprising of three dimensional germanium (Ge) quantum dot lattices formed by nitrogen (N) assisted magnetron sputtering deposition in alumina (Al_2O_3) matrix have been studied for light harvesting purposes. In order to expand the application of this material it is necessary to reduce germanium oxidation and to achieve stabilization of germanium/alumina interface. [1,2] Effects of tuning the nitrogen concentration, substrate temperature and Ge sputtering power during the films preparation are monitored. It is shown that the N presence not only reduces germanium oxidation during annealing but also affects the size and arrangement of germanium quantum dots. Deposition temperature and Ge sputtering power affect Ge quantum dot size, separation and the regularity of their positions. Consequently, optical and electrical properties of the films, especially their photo-current, strongly depend on the deposition conditions. Additionally, the film deposited at 500 °C shows the multiple exciton generation and significant photo response, so it could be used as a sensitive layer for photodetectors or photovoltaic light harvesting devices. We have shown how to manipulate the photogeneration properties and its dependence on the light energy by materials structure, especially on the Ge QD size and its internal structure. The above mentioned effects and the material itself could be very useful in light harvesting and production of heavy –metal free high-efficient solar cells.

Acknowledgements

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T8: Semiconductor, dielectric & piezoelectric thin films

Synthesis of nanostructured zinc oxide films

Em Jen P. Arce[1], *Maria Theresa G. De Leon*[2], *Marc D. Rosales*[2], *Tomohiro Yamaguchi*[3], *Magdaleno R. Vasquez Jr.*[1*]

[1]Department of Mining, Metallurgical and Materials Science Engineering,
Univ. of the Philippines- Diliman, Quezon City, Philippines
[2]Electrical and Electronics Engineering Institute, Univ. of the Philippines-Diliman, Quezon City, Philippines
[3]Graduate School of Engineering, Kogakuin University, Tokyo, Japan
[*]E-mail: mrvasquez2@up.edu.ph

Keywords: zinc oxide film, piezoelectric film, nanostructured film

To support the “zero power requirement” (10 to 1000 mW) of wireless sensor networks, conventional batteries are currently used. However, due to their limitations, research and development activities are continuously being done to determine alternative sources that can provide perpetual energy with minimal human intervention as well as environmentally sustainable. Energy harvesting that harnesses energy from ambient sources and converts them to electrical energy has recently attracted attention especially on the use of piezoelectric materials. Among the materials of significant interest is zinc oxide (ZnO). Piezoelectricity in ZnO is highly dependent on the formation of the wurtzite structure [1]. In this study, ZnO films with MIN and MAX setting (Table 1) were synthesized via sol-gel spin coating technique. Prior to deposition using spin coating, metal coated glass substrates were ultrasonically cleaned. The process of ZnO film deposition is depicted in Fig.1. After deposition, films were subjected to Raman spectroscopy, x-ray diffraction, and scanning electron microscope for compositional and morphological characterizations.

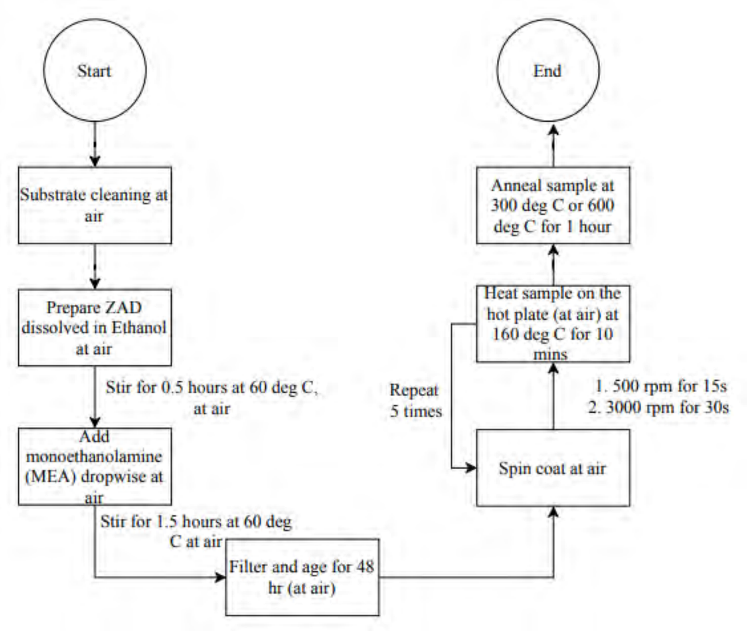

Figure 1. The ZnO film deposition process.

Table 1. Parameters for ZnO film formation.

Factor	MIN	MAX
Precursor Concentration	0.3M	0.6M
Molar ratio ([MEA]/[ZAD])	1	1.5
Annealing Temperature	300°C	600°C

Acknowledgments

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Determination of complex dielectric function of ion-bombarded amorphous germanium by spectroscopic ellipsometry

Tivadar Lohner[1], Edit Szilágyi[2], Zsolt Zolnai[1], Attila Németh[1], Péter Petrik[1], Zsolt Fogarassy[1], Levente Illés[1], Endre Kótai[2], Miklós Fried[1]*

[1]Institute of Technical Physics and Materials Science, Centre for Energy Research,
Hungarian Academy of S ciences, Konkoly Thege Miklós út 29-33, H-1121 Budapest, Hungary
[2]Institute for Particle and Nuclear Physics, Wigner Research Centre for Physics,
Konkoly Thege Miklós út 29-33, H-1121 Budapest, Hungary
[*]E-mail: lohner.tivadar@energia.mta.hu

Keywords: ion-implantation, germanium, spectroellipsometry, ion beam analysis, electron microscopy

Measuring with spectroscopic ellipsometer (SE) in the light wavelength range from 190 to 1690 nm we determined the complex dielectric function of fully amorphized germanium layer produced by two-step aluminum ion implantation (120 keV and 300 keV). The amorphous layer formed by the first step ion implantation will make practically impossible the partially channelled condition for the second ion implantation step. The reason for selecting a relatively light mass projectile (Al) was to avoid void formation in case of implantation of heavy mass ions. The evaluation of the multiple angle of incidence ellipsometric spectra was performed using a two-layer optical model: a fully amorphized germanium layer with a germanium oxide surface layer. The complex dielectric function of fully amorphized germanium has been modelled using the Tauc-Lorentz or the Cody-Lorentz dispersion relations. The generated ellipsometric spectra were fitted to the measured ones using a regression algorithm. The measure of the fit quality is the mean square error.

The thickness of the fully amorphized germanium layer has been determined by Rutherford Backscattering Spectrometry (RBS) in combination with channeling and by cross-sectional transmission electron microscopy (XTEM). The thickness values evaluated from SE, RBS and XTEM measurements (678.9±0.1 nm, 659±33 nm, 680 nm, respectively) are similar within the experimental uncertainty. In addition, dispersions of refraction indices, n and extinction coefficient, k were also determined. It was found that the Cody-Lorentz dispersion relation is more appropriate for the evaluation of the spectroellipsometric measurements on implantation amorphized germanium than the Tauc-Lorentz relation.

Spectroscopic study of spin-coated MoS_2 films

Grazia Giuseppina Politano[1*], *Marco Castriota*[1,2], *Maria Penelope De Santo*[1,2],
Mario Michele Pipita[3], *Giovanni Desiderio*[2], *Carlo Vena*[1], *Carlo Versace*[1,2]

[1]Dipartimento di Fisica, Università della Calabria 87036 Rende CS, Italy
[2]Licryl CNR/Nanotec c/o Dipartimento di Fisica, Università della Calabria 87036 Rende CS, Italy
[3]Notredame s.r.l., c/o Dipartimento di Fisica, Università della Calabria, Italy
[*]E-mail: grazia.politano@unical.it

Keywords: ellipsometry, molybdenum disulfide, optical properties

In the field of Transition Metal Dichalcogenides (TMDCs), molybdenum disulfide (MoS_2) has attracted an outstanding interest due to several applications. MoS_2 has potentialities not yet fully realized in solution-based applications. However, the lack of knowledge of the optical properties of MoS_2, especially in the infrared range, has significantly limited his use in many exciting photonic fields. In this work, the broadband optical properties of MoS_2 films deposited by spin-coating onto Si/SiO_2 substrates were studied by means of Variable Angle Spectroscopic Ellipsometry (VASE).

The structural properties of the samples were investigated by Micro-Raman Spectroscopy.

The optical properties of the films show a mid-gap state at~ 0.6 eV, not reported in an ellipsometry work before, induced by defects in the MoS_2 samples.

Magnetron sputtering deposition of core/shell Ge/Al quantum dot lattices in amorphous Al_2O_3 matrix

Ivana Šarić[1*], *Marija Tkalčević*[1], *Lovro Basioli*[1], *Sigrid Bernstorff*[2], *Maja Mičetić*[1]

[1]Ruđer Bošković Institute, Bijenička cesta 54, 10000 Zagreb, Croatia
[2]Elettra sincrotrone, S.C.p.A., Strada Statale 14 km 163,500 in AREA Science Park, Basovizza/Trieste 34149, Italy
[*]E-mail: Saric.Ivana@irb.hr

Keywords: germanium quantum dots (QDs), core – shell QDs, magnetron sputtering

In this work, thin films of core/shell Ge/Al quantum dots embedded in Al_2O_3 matrix were investigated. Thin films were produced by a magnetron sputter deposition of the Ge/Al/Al_2O_3 multilayer. Two series were explored. In the first series we have tuned the Ge core size by varying the Ge-layer deposition time while the other parameters were kept constant. In second series we have added an additional shell of Si_3N_4 in order to further enhance the spectral response. Structural properties were investigated using GISAXS (Grazing incident small angle X-ray scattering) method. The method confirmed the formation of core/shell quantum dots, differing by the sizes of the core and shell, that are arranged in a 3D-ordered network. The optical properties of the materials, their photo-generation ability and spectral response show strong dependence on the germanium core size, as well as on addition of Si_3N_4 shell. The materials are interesting for application is solar cells, photodetectors and sensors.

Acknowledgements:
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Thin ferroelectric films on semi-insulating silicon carbide for tunable high power applications

Andrei Tumarkin, Alexander Gagarin, Michail Zlygostov, Evgeny Sapego,*
Andrei Altynnikov, Andrei Kozyrev

Saint-Petersburg Electrotechnical University, Saint-Petersburg, Russia
*E-mail: avtumarkin@yandex.ru

Keywords: ferroelectric films, silicon carbide, high power microwave applications

Ferroelectrics (FE) in a paraelectric state, especially barium-strontium titanate $Ba_xSr_{1-x}TiO_3$ (BST), have received much attention as promising material for tunable microwave (MW) devices. However, tuning under high power can lead to the nonlinear distortion of the operating signal, due to the overheating of the FE material. The usage of MW devices based on the FE film deposited on a high heat conducting substrate should radically increase the power of working MW signal as compared to semiconductor elements. In this context, the present work considers the possibility of oriented growth of BST ferroelectric films on semi-insulating silicon carbide (SiC) substrates and their structure and microwave characteristics.

Thin BST films on SiC substrates were obtained by RF magnetron sputtering of $Ba_{0.4}Sr_{0.6}TiO_3$ target. The structure and microwave properties of the BST films on silicon carbide were substantially improved by using the intermediate annealing, i.e. depositing an initial BST layer, “in situ” annealing, then depositing of a second BST layer, and so on in order to reach the targeting thickness of multi-layered structure [1]. The phase composition of obtained BST films was studied by X-ray diffraction (XRD). The microstructure and surface morphology were studied by atomic force microscopy. The component composition of the BST films was evaluated using the medium energy ion scattering method.

According to XRD analysis, the multi-layer BST thin film prepared with the using of intermediate annealing shows highly (h00) oriented perovskite structure while the single-layer film is polycrystalline. The difference in crystal lattice between the multi-layer and the single-layer BST film can be explained by the fact that during the multi-layered film preparation the each annealed layer begins to play the role of a new substrate. In this case, there are two reasons for the oriented growth: the low supersaturation and the absence of an interphase energy barrier, since the new layer is formed on its own material.

The capacitor based on the highly oriented BST/SiC heterostructure demonstrate a tunability more than two times at an electric field strength of 50 V/μm, and a Q-factor of not lower than 50 at a frequency of 2 GHz, giving the best combination of tunability and losses for BST/SiC structures at microwaves.

Microwave investigation of the BST capacitors was performed at the elevated MW signal up to 10 W of the reactive power on the capacitor. Observed deformation of the resonant curve (due to the capacitance deviation under the high MW signal) has demonstrated that the power handling capability of the FE tunable capacitors on the SiC substrate is limited by the electric non-linearity, not the overheating. Thus, the integration of ferroelectric BST films with semi-insulating SiC would be a promising route for the development of tunable high-power microwave devices.

Acknowledgments

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Thin ferroelectric coatings on silicate porous glass for tunable microwave applications

Andrei Tumarkin[1], Natalia Tyurina[2], Zoya Tyurina[2], Sergey Sviridov[2], Olga Sinel'shchikova[2], Alexander Gagarin[1], Evgeny Sapego[1]*

[1]Saint-Petersburg Electrotechnical University, Saint-Petersburg, Russia
[2]Institute of Silicate Chemistry, Saint-Petersburg, Russia
*E-mail: avtumarkin@yandex.ru

Keywords: ferroelectric films, porous glass, metamaterials, microwave applications

Ferroelectrics (FE) in a paraelectric state have received much attention as promising material for tunable microwave (MW) devices. One of the promising ways to improve functional characteristics of ferroelectric materials is the creation of composite elements using ferroelectric coatings on porous matrices. The advantage of this approach is the ability to create new multicomponent materials with previously unattainable properties, in particular, metasurfaces. Oxide glass with a porous structure has a number of advantages compared to other porous materials: thermal, chemical, and biological stability. In this context, the present work considers the possibility of creating ferroelectric tunable structures based on silicate glasses with a porous structure.

For obtaining porous glass by the method of ion exchange, potassium iron-containing silicate glasses (KFeSi) are used in the work. According to X-ray diffraction analysis in the tempered and annealed glass of the KFeSi composition, the crystalline phase of Fe_3O_4 is formed, the presence of which indicates that the glasses under study have magnetic properties. For the formation of the porous structure, the synthesized glass were subjected to ion exchange in molten $LiNO_3$ and $NaNO_3$ in the temperature range of 350–500°C with isothermal aging for 2–24 hours.

On the basis of porous glasses obtained by ion exchange, glass structure coated by barium-strontium titanate was synthesized by impregnation of glass substrate with a sol prepared by the glycine-nitrate technique. Results of X-ray diffraction confirm the presence of barium-strontium titanate on the surface of the glass and in the pore space of the material. According to XRD data, the obtained dense glass/ferroelectric samples contain $Ba_{0.75}Sr_{0.25}TiO_3$, Fe_3O_4 and poly-BaTiO. Some samples were additionally annealed in oxygen atmosphere in order to improve crystal lattice of barium-strontium titanate. XRD analysis of annealed structures showed the increasing of peak's intensity confirming the improvement of crystal structure of barium-strontium titanate.

For the estimation of the dielectric permittivity of the synthesized samples a segment of the microstrip transmission line connected to the vector network analyzer was used. In the experimental study the samples were incorporated to the transmission line and the frequency dependences of the reflection coefficient module and the phase of the transmission coefficient were measured; the measurement data were converted into dielectric permittivity. The data of the measurements indicated: 1) the effect of ferroelectric coating on the dielectric permittivity of the samples; 2) the increasing of dielectric permittivity, tunability and the decreasing of dielectric losses of samples after the annealing.

Acknowledgments

This work was supported by RFBR projects 19-07-00600, 19-37-90055.

T9: Magnetic, superconducting and multiferroic thin films

Formation of cobalt doped lead ferrite ($Pb_2Fe_2O_5$) thin films by reactive magnetron sputtering and investigation

Benas Beklešovas[*], *Vytautas Stankus*

Department of Physics, Kaunas University of Technology, Kaunas, Lithuania
[*]E-mail: benas.beklesovas@ktu.edu

Keywords: multiferroics, cobalt, doping, lead ferrite, reactive magnetron sputtering, ferroelectric

Multiferroics exhibit more than one primary ferroic property simultaneously. These materials could display coupled ferromagnetic, ferroelectric and ferroelastic orderings features in a same phase. The coexistence of several order parameters brings out the possibility for developing new applications such as multiferroic random access memories and multi-state memories (MRAMs, FeRAMs), photovoltaic solar cells, sensors and other high-tech electronics [1]. Due to its complex multifunctional mechanisms multiferroics are rare materials. There are even less multiferroics which exhibit its unique properties at room temperature. Therefore, the need to search for new materials and improve existing ones is only increasing.

One of the little researched multiferroics is lead ferrite – $Pb_2Fe_2O_5$ (PFO). Min Wang et al. in his work investigated lead ferrite bulk ceramics and characterized its multiferroic properties [2]. Thus, these results draw attention for further investigation. Our research group have investigated PFO phase in form of thin films synthesized by reactive magnetron sputtering deposition in oxygen environment. During this research we confirmed that PFO exhibits multiferroic properties. P-E measurements showed unsaturated hysteresis loops which could be affected by the leakage currents in thin film samples because of non-stoichiometric and defects existence. Hence there is a need of improving of these materials which could be achieved by other elements substitution. For this purpose, we have selected cobalt ions as dopants. Co is ferromagnetic material and is one of the promising elements for improvement of ferromagnetic properties of doped PFO thin films. Fe^{3+} ions are substituted by $Co3^{+}$ ions which have similar ionic radius of 0.645 Å and 0.61 Å respectively. In this work the *in-situ* layer by layer reactive magnetron sputtering synthesis method was used. Acquired results of cobalt doped lead ferrite shows the formation of multiferroic properties and structure.

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T10: Thin films for optoelectronics, nanoelectronics, spintronics and batteries

Crystallisation of ALD Ga_2O_3 films

Zsófia Baji, Zoltán Szabó, Ildikó Cora*

Institute of Technical Physics and Materials Science, Centre for Energy Research, Hungarian
Academy of S ciences, Konkoly Thege Miklós út 29-33, H-1121 Budapest, Hungary
*E-mail: baji.zsofia@energia.mta.hu

The present work focuses on the deposition, and heat treatment of Ga_2O_3 films with atomic layer deposition (ALD). ALD is a self-limiting layer by layer growth method based on the consecutive chemisorption of precursor gases on a heated substrate surface resulting in a uniform and conformal coverage and a mono-layer by mono-layer growth even on high aspect ratio or nanostructured surfaces.

Ga_2O_3 is a wide band-gap semiconductor very promising due to its photocatalitic properties, gas sensing properties as well as its possible applications as UV transparent conductive oxide. The present work uses a novel Ga precursor, hexakis-dimethylamino-digallium, which facilitates the use of a wider ALD window than the commonly used precursors (between 130°C and 270°C). The Zn doping was performed using diethylzinc, and water was used as an oxidant.

As ALD deposited Ga_2O_3 films are always amorphous, a number of different heat treatments were used to achieve crystalline β- Ga_2O_3. The films were deposited with a Picosun Sunale R-100 reactor, the morphology of the layers was characterised with atomic force microscopy, the crystal structure and orientation were examined by transmission electron microscopy, and transmission measurements were conducted. The heat treatments of the samples were attempted by rapid thermal annealing and by longer annealing procedures in a furnace. The temperature range was between 700° and 900°C and the used atmosphere was oxygen or nitrogen. As the crystallisation of the films was hard to initiate, a detailed TEM examination was conducted to explain the physical phenomena behind this behaviour

Pulsed laser deposition of highly conductive In:ZnO films

Jaroslav Bruncko[1], Marie Netrvalova[2], Pavol Sutta [2], Andrej Vincze[1], Miroslav Michalka[1], Jaroslav Kovac, jr.[3]*

[1]International Laser Centre, Ilkovicova 3, 841 04 Bratislava, Slovak Republic
[2]University of West Bohemia – New Technologies – Research Centre, Univerzitni 8, Plzen, The Czech Republic
[3]Institute of Photonics and Electronics, Faculty of Electrical Engineering and Information Technology, Slovak University of Technology, Ilkovicova 3, Bratislava, Slovak Republic
[*]E-mail: jaroslav.bruncko@ilc.sk

Keywords: zinc oxide, transparent conductive oxide (TCO), indium doping, thin film, pulsed laser deposition

Many kinds of TCO have been investigated in recent years and new perspective candidates have been practically applied but the zinc oxide (ZnO) materials are considered as the most perspective [1]. In comparison with traditionally used ITO, ZnO is cheaper, its natural sources are abundant and material itself and its treatment is not connected with considerable health hazard. Pure, undoped ZnO exhibits excellent transparency in VIS region but rather poor electrical conductivity so efficient doping for increasing conductivity with parallel preserving optical transparency attracts huge scientific interest. Mixing with other elements provides increasing of electrical conductivity or band-gap energy affecting. There are widely accepted agreement that metal elements of the group III (Al, Ga and In) provide the best results in decreasing of natural ZnO resistivity.

The contribution deals with In doped ZnO films (0.15, 1.0 and 2.0 wt. % of In_2O_3) prepared by pulsed laser deposition (PLD). Deposition temperature was 400 °C and ambient consisted of pure O_2 at 3.0 Pa. Thin layer of pure Zn was deposited on substrate surface before growth of ZnO films (or on final surface after deposition respectively) for reducing of Zn vacancies [2] and annealed at 400 °C.

Investigation by SEM and XRD confirmed columnar structure of prepared films with highly uniform crystallographic orientation regardless of applied deposition parameters. Samples exhibited high optical transparency in VIS region with sharp absorption edge near 380 nm and band gap energies varied between 3.16–3.20 eV at room temperature. Depth profile of In concentration analysed by Secondary Ion Mass Spectroscopy (SIMS) exhibited constant content of In and other elemental constituents over the layer depth. Room-temperature photoluminescence (PL) was measured with HeCd laser at 325 nm. In comparison with undoped ZnO, In:ZnO all emission records consisted of an intense peak around 380 nm while the emission in visible region (450–700 nm) was negligible which suggest low population of crystal structure. The electrical properties of In:ZnO films (resistivity, carrier concentration and Hall mobility) were investigated by Hall measurement device (4–points van der Pauw method) at room temperature. In doped samples resistivity increased in 3 orders (up to 10^{-4} Ω.cm) in comparison with undoped ZnO. All doped samples exhibited high conductivity and very stable behaviour regardless of doping concentration.

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Pulsed laser deposition of high-transparency molybdenum oxide thin films

Eva Horynova[1], Josef Sedlacek[1], Lucie Abelova[1], Lukas Horak[2], Jakub Holovsky[1,3]*

[1]Department of Electrotechnology, Czech Technical University in Prague, Czech Republic
[2]Department of Condensed Matter Physics, Charles University, Prague, Czech Republic
[3]Institute of Physics CAS v. v. i., Prague, Czech Republic
[*]E-mail: eva.horynova@fel.cvut.cz

Keywords: transparent metal oxide, pulsed laser deposition, optical spectroscopy, photothermal deflection spectroscopy

Molybdenum oxide is a transition metal oxide with one of the most widespread applications. In general, transition metal oxide can be used in solar cells, flat panel displays, sensors, and more. What makes molybdenum oxide one of the most popular amongst the transition metal oxides are its remarkable physical and chemical characteristics such as high work function bigger than 5 eV [1]. We achieved molybdenum oxide thin layers with exceptionally high transmittance in the visible spectra. Samples were prepared by pulsed laser deposition, which main advantage is the precise control of deposition parameters. The substrate temperature and oxygen pressure were changed in the case of deposition from molybdenum trioxide target. There were also some samples prepared from a pure molybdenum target, and mostly oxygen pressure was the variable in this case. Photothermal deflection spectroscopy and ellipsometry were mainly used for obtaining optical characteristics such as the transmittance, refractive index, absorption coefficient, Urbach energy, and bandgap. The crystallinity of the layers was analyzed by X-ray diffraction and it showed dependence between the substrate temperature and the crystallinity of the layer. Lastly, the samples were contacted and measured with the Van der Pauw method in order to acquire the resistivity.

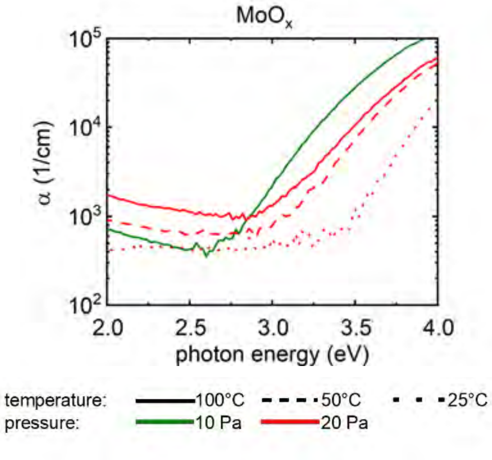

Figure 1. Absorption coefficient of molybdenum oxide layers measured by photothermal deflection spectroscopy for the temperatures 25°, 50° and 100°C and the pressures 10 Pa and 20 Pa

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High performance supercapacitors based on Ni(O, S, S_2) hollow microspheres

Behnam Eshqi[1], *Mohammad Qorbani*[2], *Alireza Z. Moshfegh*[1,3*]

[1]Department of Physics, Sharif University of Technology, Tehran, Iran
[2]Center for Condensed Matter Science, National Taiwan University, Taipei, Taiwan
[3]Institute for Nanoscience & Nanotechnology, Sharif University of Technology, Tehran, Iran
[*]E-mail: moshfegh@sharif.edu

Keywords: nickel chalcogenide, supercapacitor, hydrothermal, nickel foam

Supercapacitors, have attracted great attention because of their outstanding power density, excellent reversibility and very long cycle life. [1] Moreover, transition metal oxides/sulfides (like Nickel and Cobalt oxides/sulfides) have exhibited high specific capacitance and high energy density due to their pseudocapacitive performance. [2]

In this research, NiS_2 hollow microspheres are fabricated through a facile hydrothermal method. Then NiS and NiO microspheres prepared by calcination of NiS_2 in air at 400 ºC and 700 ºC without any morphological change, respectively. Finally, the samples transferred to a nickel foam substrate for further study. The prepared samples are characterized by SEM, TEM and EDS techniques. Based on electrochemical measurements, all three samples display pseudocapacitive behavior. Maximum specific capacitance of the NiS_2, NiS and NiO samples are calculated (at 25 $mV.s^{-1}$) of 535, 365 and 160 Fg^{-1}, respectively (Figure 1). Further investigations reveal that NiS_2 microspheres exhibit a better specific capacitance at higher scan rates because of their lower electron transfer resistance.

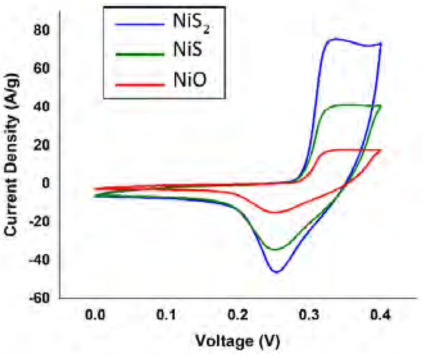

Figure 1. Cyclic voltammetry of NiO, NiS and NiS_2 electrodes at 25mV/s (Reference electrode: Ag/AgCl)

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Nanostructured silicon as potential anode material for Li-ion batteries

*Matea Raić[1,2], Lara Mikac[1,2], Mile Ivanda[1,2]**

[1]Laboratory for Molecular Physics and Synthesis of New Materials, Ruder Bošković Institute, Bijenička c. 54, 10000 Zagreb, Croatia; matea.raic@irb.hr (M.R.), lmikac@irb.hr (L.M.), Goran.Stefanic@irb.hr (G.Š.), gotic@irb.hr (M.G.)
[2]Research Unit New Functional Materials, Center of Excellence for Advanced Materials and Sensing Devices, Bijenička c. 54, 10000 Zagreb, Croatia
*E-mail: mile.ivanda@irb.hr; Tel.: +385-1-456-0928 (Corresponding author)

Keywords: silicon, porosity, anode, battery, electrochemical performance

The success of Li-ion batteries in the early 1960s took years of research and contribution of many scientists and engineers. Since then there are several electronic revolutions and still lithium-ion (Li-ion) cells are the most widely used as rechargeable battery system for portable electronic devices and electrical vehicles. It has many advantages like high energy density, long storage life, small volume, light weight, low self-discharge efficiency and non-memory effect. The most widely used anode is graphite whose lithiated compounds have stable phases up to the LiC_6 stoichiometry corresponding to a theoretical specific capacity of 372 mAh/g [1]. In contrast, silicon possesses a very high theoretical capacity of 4200 mAh/g and can intercalate 4.4 Li into Si at high temperature to form $Li_{15}Si_4$ [2]. Although silicon possesses all of these advantages, silicon based anodes suffer from huge volume expansion upon cycling (≈400%) causing electrode fracture and electrical isolation during repeated cycling [3]. Continuous volume changes cause the breaking-reformation of the solid electrolyte interphase (SEI) film which leads to consumption of lithium-ions and electrolyte. Exhaustion of the electrolyte causes the degradation of conductivity and induces fast capacity loss [4]. The porous structure can provide a large space to accommodate volume expansion and provide a large surface area for lithium-ion transport from electrolyte to silicon [5]. In this work, we studied nanostructured silicon for the possible use in anode fabrication to produce non-expensive anode material which can achieve better capacitance properties. In the present work, structural and microstructural changes in silicon nanomaterials were examined using several methods: X-ray powder diffraction combined with the results of Raman spectroscopy, FT-IR spectroscopy, UV-Vis spectrometry, Nitrogen adsorption measurements, and TEM analysis. Electrochemical performances were investigated by cyclic voltammetry and galvanostatic charge-discharge measurements

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Fabrication and characterization of CaF_2/ZnS multilayered film for improving OLED performance

Naoya Satoh, Takuya Kitabayashi, Takayuki Kiba, Midori Kawamura, Yoshio Abe, Kyung Ho Kim*

Department of Materials Science and Engineering, Kitami Institute of Technology, Kitami, 090-8507, Japan
*E-mail: tkiba@mail.kitami-it.ac.jp

Keywords: organic light-emitting diode, encapsulation, microcavity, distributed Bragg reflector

Recently, an organic light-emitting diode (OLED) is attracting attention because of their advantages such as high contrast, low cost, and application to flexible devices. But rigorous encapsulation is essential for the application of an OLED due to the use of air/moisture-sensitive materials. In this study, we fabricated inverted-type OLED (iOLED) with CaF_2/ZnS alternately deposited film and examined the multiple functionalities of the multilayered film; (1) inhibition of dark-spot formation and (2) optical high-reflection resulting narrow EL spectrum due to the microcavity effect.

All layers of OLEDs including dielectric multilayer were prepared by vacuum thermal evaporation method. Fig. 1 shows OLED structures with dielectric multilayer fabricated in this study. For comparison of protection performance, the conventional-type OLEDs (cOLED) with a dielectric single-layer of CaF_2 and ZnS were examined. In Fig.2, the decrease of emissive area due to dark-spot formation was shown. The devices were kept in the atmosphere without any further encapsulation. Deposition of both dielectric layers on the cOLED moderates the dark-spot formation after 3 days. The ZnS layer is more effective compared to the CaF_2 layer. Notably, there is no dark-spot formation in iOLED devices even after one month, which is probably because the air/moisture sensitive film (Al, LiF) was protected from the atmosphere by inverted structure and further covering by dielectric multilayers. The current-voltage-luminance characteristics and EL spectra of all OLEDs were measured. EL spectra of iOLED with different pairs of CaF_2/ZnS multilayered film showed significant narrowing depending on the increase of the pair numbers, indicating the microcavity effect of the dielectric multilayer acting as a reflective mirror.

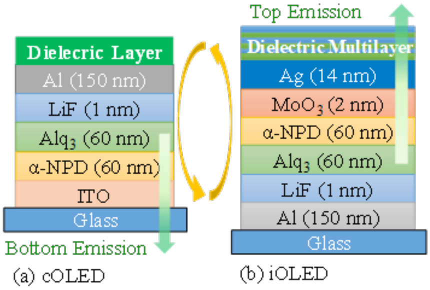

Fig. 1. The typical device structures of (a) conventional OLED and (b) inverted OLED.

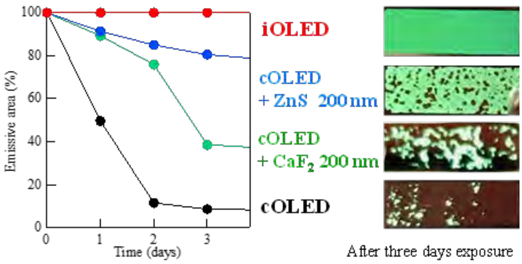

Fig. 2. Degradation of emissive area as a function of storage day. Pictures show sample pixels (2×5 mm^2) of OLEDs after three days exposure to the atmosphere.

Acknowledgments

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ZnO as transparent and conductive oxide versus diamond thin films for PIN diodes based on a-SiC:H deposited at temperatures between 350–450 °C

The Ha Stuchlíková[*]*, Jan Čermák, Oleg Babčenko, Zdeněk Remeš, Alexander Kromka, Jiří Stuchlík*

Institute of Physics, Czech Academy of Sciences, Cukrovarnická 10, 16200 Prague 6, Czech Republic
[*]E-mail: hotheha@fzu.cz

Keywords: ZnO, diamond thin films, a-SiC:H, thin film diodes

Indium tin oxides (ITO) or doped zinc oxides (ZnO) are commonly used as transparent and conductive oxides (TCO). They are stable for the deposition of standard device-quality a-Si:H thin films at 220 °C. However, they are not stable enough for a consequent deposition of additional thin films at higher temperatures that are required for innovative structures with improved optical and electrical properties. For example, in the case of a novel a-SiC:H diode deposited by plasma enhanced chemical vapour deposition (PECVD) at surface temperature 400 °C [1, 2] the substrates coated by boron-doped diamond (BDD) had to be used [3, 4].

In this study, we tested temperature stability of aluminium doped ZnO thin films and compare them with nano-crystalline diamond (NCD). The NCD films were deposited at temperature 450 °C. Both types of thin films evince high transmission and a good scattering of light via their high roughness. The surface morphology of the layers before and after aneeling in high vacuum in the range from 350 to 450 °C were characterized by scanning electron microscopy and atomic force microscopy. As well as the changes of optical transmissions and electrical conductivities were studied. Finally, a-SiC:H diode structures were fabricated on the aneeled films and characterized by I-V measurements.

Acknowledgaments

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Fabrication and optical characterization of Al nanomesh structure by nanosphere lithography

Mai Ugajin[1], Natsumi Iijima[1], Takayuki Kiba[1], Midori Kawamura[1], Yoshio Abe[1],*
Kyung Ho Kim[1], Yafeng Chen[2], Junichi Takayama[2], Satoshi Hiura[2], Akihiro Murayama[2]

[1]Department of Materials Science and Engineering, Kitami Institute of Technology, Kitami, 090-8507, Japan
[2]Faculty of Information Science and Technology, Hokkaido University, Sapporo, 060-0914, Japan
[*]E-mail: tkiba@mail.kitami-it.ac.jp

Keywords: nanosphere lithography, Al nanomesh, transparent electrode

The practical use of an organic light-emitting diode (OLED) is now spreading in a television, smartphone display, and wearable devices. The light-extraction of the guided-mode in the interface of OLED structure is crucial for improving external quantum efficiency, thus the nanostructured transparent electrode can be the one solution for that. In this study, we fabricated Al nanomesh structure by nanosphere lithography (NSL) method and evaluated its characteristics as transparent electrodes for OLED.

Fig. 1 shows the fabrication process of the Al nanomesh structure. Two-dimensional alignments of polystyrene (PSt) beads on the glass substrates were reduced its diameters by a reactive ion etching (RIE). Subsequently, Al thin films of 50 nm thickness were deposited by vacuum thermal evaporation. Al nanomesh structure was obtained by the lift-off process by sonication. We fabricated Al nanomesh structure with PSt beads in diameter of 350 and 500 nm (Ps350 and Ps500) which determine the period of holes array, and with different RIE treatment times which defines hole diameter. Here, we defined a parameter, fill-factor (FF), describing the proportion occupied by the metal portion of Al nanomesh.

Fig. 2 shows the transmission spectra of Al nanomesh with different hole period and FF. Peak positions in the transmittance spectra coincided among the same hole-periods nanomesh and red-shifted by enlarging the hole-periods, whereas its transmittance was changed depending on the FF. The sheet resistance of fabricated Al nanomeshes was lower than 65 Ω/sq with Ps350, FF0.25, indicating the possible use for OLED transparent electrodes. The light-extraction property of Al nanomeshes with Alq_3 film, which is typical emissive materials for OLED, was also examined.

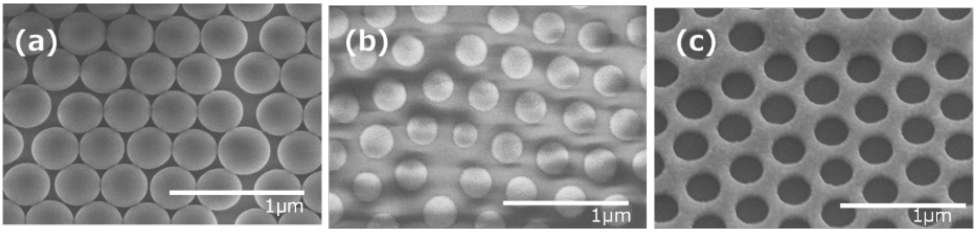

Figure 1. SEM images of the PSt beads arrangement (a) before and (b) after the RIE treatment, and (c) the fabricated Al nanomesh with FF 0.55 and 350 nm hole-periods

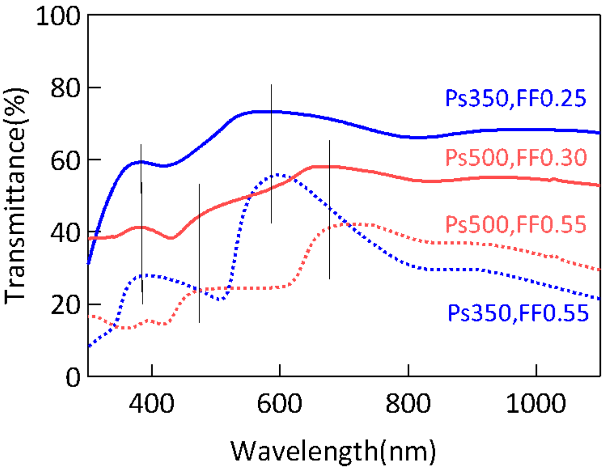

Figure 2. Transmission spectra of Al nanomesh with different hole-periods and FF.

Acknowledgments

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SIMS investigation of organic layer structures

Andrej Vincze[1*], *Martin Weis*[2]

[1]International Laser Centre, Ilkovicova 3, 841 04 Bratislava, Slovakia
[2]Institute of Electronics and Photonics, FEI, Slovak University of Technology, Ilkovičova 3, 812 19, Bratislava, Slovakia
[*]E-mail: andrej.vincze@ilc.sk

Keywords: organic materials, SIMS, OLED structures

The organic materials are matured for recent days, and there are many applications of them. The simple organic layer structures as Organic Light Emitting Diodes (OLED) are close to take the leadership in everyday's use. The OLED fabrication process is much simpler as concerning the laboratory conditions for inorganic counterparts; however the OLEDs need to be packaged well enough to prevent their degradation. The degradation may be caused mainly by the light, water, and oxygen. The degradation evaluation is often correlated to the lifetime, which is recently almost at values ~20.000 hours of operation [1]. The first attempt for OLED was used Alq3 and diamine as organics, which were sandwiched between ITO and Mg:Ag contacts in 1987 [2]. At that time also the degradation was investigated with recognized drive voltage increase and reported the 30% loss in 10 hours under constant current drive. Nearly 30 years later, the OLED technology matured, however the major problem is still the stability without proper packaging. One way of lifetime exploration is possible by constant voltage/current stress applied to the OLED structure and search for correlation of these results with SIMS depth profiling before and after the stress process. These processes result in various changes in device properties, most notably in the colour, luminance, current−voltage characteristic of OLEDs. Typically, the degradation manifests as a continuous loss of the device efficiency (primarily observed as the decrease of brightness at constant current or voltage) [3–5].

Our aim is to look for chemical reactions by comparison of the OLED structures without any cover layer or another prevention by SIMS depth profiling. The OLED structures were prepared on the model structure Ag/Ca/Alq3/alpha-NPD/ITO. The contribution is discussing the OLED structures without any cover layer degradation under constant current stress applied and the approach with SIMS depth profile analysis. The shown examples are describing, which changes we can expect.

Acknowledgments
The research leading to these results has received funding from the projects of APVV 17-0501 and VEGA 1/0929/17.

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T11: Thin film solar cells – inorganic, organic, perovskites etc

Microscopy of ALD grown FeS layers

Zsolt Fogarassy[1], Ildikó Cora[1], Zsófia Baji[1], Csaba Dücső[1], Béla Pécz[1]*

[1]Institute of Technical Physics and Materials Science, Centre for Energy Research, Budapest, Hungary
*E-mail: coraildiko@gmail.com

Keywords: ALD, Fe-sulphides, TEM

The growth of metal chalcogenides in the form of thin films, especially iron sulfides has attained much technological interest owing to their possible use in modern optoelectronic devices[1], biological applications[2] and solar energy[3,4]. Iron sulfide, which has a high optical absorption coefficient, is therefore expected to be applied to a light receiving and emitting device.

Fe-sulphide thin film was deposited by atomic layer deposition (ALD) technique based on [5]. In the case of Fe more precursors (Fe(acac)$_3$, Fe^{III}-trifluoropentadionate and Fe^{III}-hexafluoropentadionate) were tried, however the deposition was successful only with Bis(N,N'-di-t-butylacetamidinato)iron (II) precursor. In the case of S we used H_2S as precursor. 100 nm thick layers were deposited at 400°C, 300°C and 250°C onto different types of substrates ((001) sapphire, (111) silicon, amorphous glass). All the layers are polycrystalline. The EDS measurements confirmed that the chemical composition fluctuates around FeS. TEM confirmed that the layer has a troillite or 2H pirrhotite structure. In the case of sapphire substrate the polycrystalline layer is more textured, even more at higher deposition temperatures; [001] α-Al_2O_3 || [001] FeS.

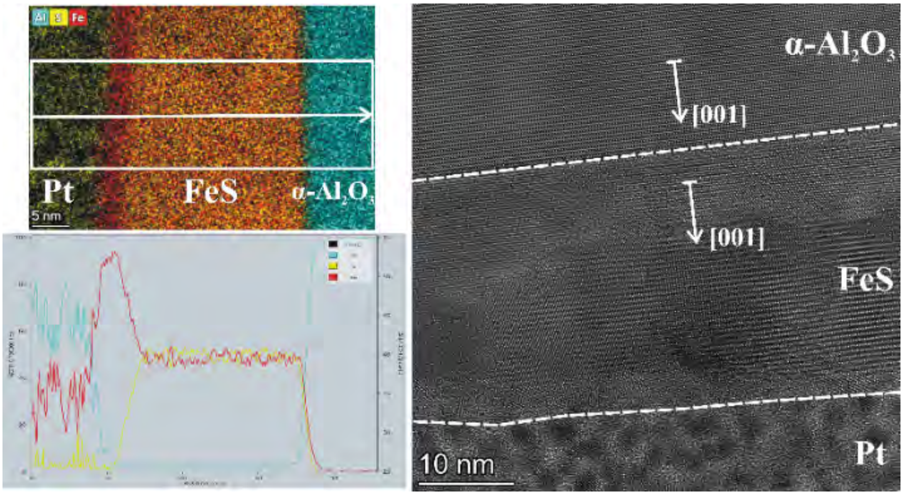

Figure 1. (Left) EDS map and line profile from the FeS layer deposited by ALD onto α-Al_2O_3. The composition of the FeS fluctuates around 1:1 ratio. (Right) HRTEM image shows that the layer is slightly textured, since [001] α-Al_2O_3 || [001] FeS.

Acknowledgments

This work is supported by the projects VEKOP-2.3.3-15-2016-00002 and VEKOP-2.3.2-16-00011. Zs. Baji thanks the Hungarian National Science Fund OTKA (Grant No. PD 116579) for the support.

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T12: Thin film sensors & actuaators

Fast timing detection of charged-particle induced radioluminescence from perovskite quantum dots

Csaba Buga, Mátyás Hunyadi, Lóránt Csige, Attila Csík*

Institute for Nuclear Research, Debrecen, Hungary
*E-mail: buga.csaba@atomki.mta.hu

Keywords: quantum dots, perovskite nanocrystals, fast-timing detectors, particle radiation

Luminescent quantum dots (QD) are promising candidates for high-precision timing detectors due to their subnanosecond optical response to exposure of charged particle beams like protons or alpha particles. Perovskite nanocrystals are particularly attractive, since they exhibit unique charge carrier dynamics, which leads to superior optoelectronic features with respect to conventional semiconductors. Furthermore, their compositional versatility, reliable operation and facile synthesis may open a gateway toward engineering of new functionalities in sensor technologies. The assembly of packed QD monolayers on photon detectors preferentially operating in avalanche mode may overcome most of the technical obstacles and restrictions in nuclear and particle physics experiments that often require high-precision time-of-flight (TOF) or high-frequency coincidence measurements with suppressed dead-time.

Inorganic $CsPbBr_3$ perovskite nanocrystals were synthesized in the size range of 8-16 nm (insert in Fig. 1), which were deposited on a glass substrate mounted on the long face of a glass prism, which was optically coupled to two photomultiplier tubes (PMTs) along its short faces. The perovskite sample was irradiated with an Am-241 open source emitting alpha particles around 5.5 MeV. The timing characteristics of radioluminescent signals and quantum yields were investigated from the coincidence data recorded with high-sampling rate digital shape analyser.

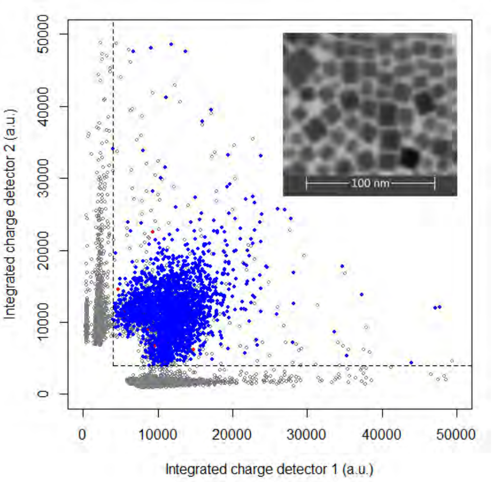


Figure 1. Scatter plot of integrated charges measured with two PMTs following the irradiation of perovskite nanocrystals with 5.5-MeV alpha particles from Am-241 source. Coincident light signals from the perovskite nanocrystals are plotted as blue dots. Insert: transmission electron microscopy image of the $CsPbBr_3$ perovskite nanocrystals.

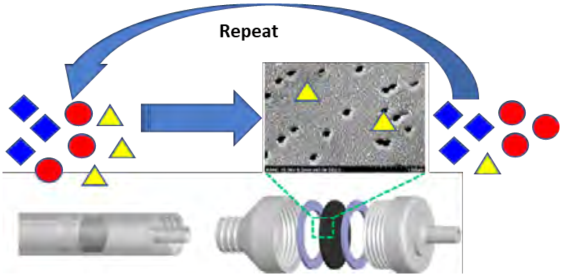
A syringe filter type plasmonic biosensor

Nak-hyeon Kim, Hyung Jin Kim[*]

Digital Health Care Research Center, Gumi Electronics and Information Technology Research Institute(GERI), Gumi, South Korea
[*]E-mail: hjkim745@geri.re.kr

Keywords: surface enhanced Raman spectroscopy, surface plasmon, plasmonics, biosensor, syringe filter

Raman spectroscopy is specialized in the detection and quantification of the target sample because distinctive peaks from Raman signals provide molecular identification. Despite the remarkable advantages of Raman spectroscopy, its signal is typically very weak. It is thus difficult to separate the weak Raman scattering signal from intense Rayleigh scattered light. Therefore, many researchers have investigated surface-enhanced Raman spectroscopy (SERS) for Raman signal enhancement, which is provided by plasmon resonance at metallic nanoparticles (NPs). In this study, we suggest a novel syringe-type SERS substrate with gold nanostructures. In the conventional biosensor having a substrate structure, most of the target samples do not reach the substrate surface and are discarded. However, with a syringe filter type sensor, all target samples must pass through the syringe filter, and it can be made to pass through the filter over and over again. Additionally, the gold structures that are formed on the surface of the syringe filter increase a surface reaction area and to excite a localized surface plasmon (LSP). Hot-spots at gold structures on SERS substrate finally lead to an additional enhancement of Raman scattering signal. Therefore, if this SERS sensor using a syringe is used, it is possible to detect highly sensitive biomolecules with a small number of samples.



Syringe type plasmonic sensor schematic

Acknowledgments

This work was supported by the Disaster Safety Research and Development, 20010305, Development of high-stretch material-based chemical protection suits (Level B·C class) with activity and safety through wearer's bio-signal measurement and gas detection, funded by the Ministry of Public Administration and Security.

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Photoalignment at the nematic liquid crystal - polymer interface: the importance of the liquid crystalline molecular structure

Ameer R.K. Nassrah[*]*, István Jánossy, Tibor Tóth-Katona*

Research Institute for Solid State Physics and Optics, Wigner Research Centre for Physics, Budapest, Hungary
[*]E-mail: nassrah.ameer@wigner.mta.hu

Keywords: nematic liquid crystals, photoalignment, liquid crystal – polymer interface

The alignment of nematic liquid crystals (NLCs) on solid substrates is one of the key factors in electro-optic devices. The control of surface orientation of NLCs with the help of polarized light is not only an alternative, contactless method to ensure proper alignment at the cell boundaries, but – because of its reversible character – also opens up new possibilities of applications (rewritable displays, dynamic holography etc.).

We investigate the role of the molecular structure of the NLC in the photoalignment process. For this purpose, the rigid core of the NLC has been systematically varied from biphenyl (E7 liquid crystal), through phenylcyclohexane (PCH5 and PCH7 NLCs), to bi(cyclohexane) (ZLI1695 NLC). These NLCs have been filled into special LC sandwich-cells consisting of a reference glass plate (with rubbed polyimide layer), and a photosensitive glass plate coated with PMMA polymer functionalized with azo-dye Disperse Red 1 (pDR1). Measurements on the photoalignment and photo-reorientation have been performed by the pump-probe optical setup incorporating the lock-in technique [1].

The main results can be summarized as follows: The azimuthal photoalignment extends over a wider temperature range for NLCs with phenylcyclohexane and bi(cyclohexane) rigid cores (PCH5, PCH7 and ZLI1695) than that for NLC with biphenyl core (E7) – see *Figure 1* (on a scale relative to the clearing temperature of the NLCs, T_{NI}). In contrast to NLCs with biphenyl rigid core, where zenithal (out-of-plane) photoalignment has also been measured previously [2], no such photoalignment process is detected in NLCs with phenylcyclohexane and bi(cyclohexane) rigid cores.

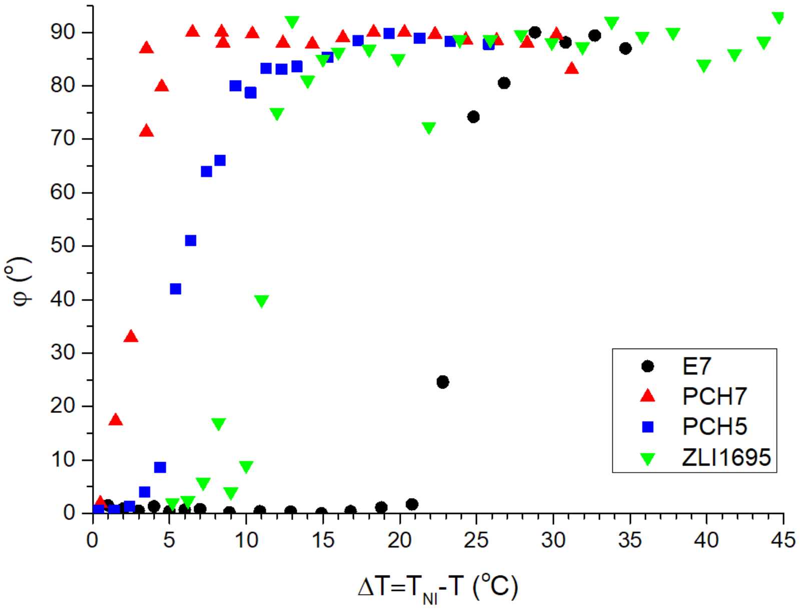

Figure 1. Temperature dependence of the azimuthal photo-reorientation angle ϕ, measured in cells filled with various NLCs as indicated in the legend.

Acknowledgments

Financial support from the National Research, Development and Innovation Office (NKFIH) Grant No. FK 125134 is gratefully acknowledged.

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T13: Vacuum Science & Technique

Measurements of virial coefficients of helium, argon and nitrogen for the needs of static expansion method

Yllka Delija, Sefer Avdiaj[*]

Department of Physics, University of Prishtina, Prishtina 10000, Kosovo
[*]E-mail: efer.avdiaj@uni-pr.edu

Keywords: virial coefficient, helium, argon, nitrogen, primary method

Generally, there are three primary methods in vacuum metrology: mercury manometer, static expansion method and continuous expansion method. For the pressure below 10 Pa, the idea of primary standard is: the gas is measured precisely at a pressure as high as possible, and then the gas is expanded to the bigger volumes and the expanded pressure is possible to be calculated. An important parameter which needs to take care in primary vacuum calibration methods is the compressibility factor of the working gas. The influence of virial coefficients on the realization of primary standards in vacuum metrology, especially in the realization of static expansion method is very important. In this paper we will present the measured data for virial coefficients of three gases Helium, Argon and Nitrogen measured at room temperature and pressure range from 130 kPa down to 3 kPa. The purity of all gases used in this research was 5.0. The dominating term due to real gas properties arises from the second virial coefficient. The influence of higher orders of virial coefficients drops rapidly with lower pressure, particularly gas pressures less than one atmosphere. So in our calculation the series of real gas was used for the first and second virial coefficient bur not for higher orders virial coefficients.

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T15: Nanometer Structures

Investigation of generalized ellipsometry applications for the detection of structural asymmetries in Gate-all-around FET architectures

E. Balogh[*]*, D. Egri, L. Kalocsai, A. Sütő, M. Tallián, P. Basa*

Semilab Semiconductor Physics Laboratory Co. Ltd., Budapest, Hungary
[*]E-mail: emeric.balogh@semilab.hu

Keywords: nanostructures, ellipsometry, gate-all-around FETs, optical characterization

Increasing device performance in the future logic applications beyond the 5 nm technology nodes is expected to be reliant on advanced transistor architectures. Nanowire (NW) and nanosheet (NS) FETs, Forksheet FETs and Complementary FETs are the most promising gate-all-around (GAA) FET architectures considered in future generation of high-density logic applications [1]. Process control of the fabrication of such complex nanostructures relies on fast, non-destructive and precise metrology methods. Some of the most widely used metrologies for characterizing the critical dimensions of the FET structures are based on spectroscopic reflectometry or ellipsometry.

Periodic subwavelength structures - such as arrays of FETs studied in the UV to NIR spectral ranges - show optical anisotropic properties. This type of geometrical anisotropy strongly depends on the detailed structural parameters of the periodic grating [2]. Generalized ellipsometry and Mueller Matrix polarimetry are advanced versions of ellipsometry designed to characterize the anisotropic properties of materials. This sensitivity to the optical anisotropy of the studied samples makes them a strong candidate for advanced characterization techniques to be used at future technology nodes. It has already been shown that Mueller Matrix polarimetry is capable of detecting structural asymmetries, like fin bending or pitch walking, in case of FinFET architectures [3].

In this contribution we investigate by means of simulations the possibilities of using generalized ellipsometry to detect structural asymmetries in advanced transistor designs. We investigate the relations between structural asymmetry and optical anisotropic properties of the structures specific to advanced GAA FET designs, which are under development for future technology nodes.

Acknowledgments

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Polymer nanolayers for down feather surface modification

Katarzyna Bednarczyk, Marcin Libera*

Faculty of Science and Technology, Institute of Chemistry, University of Silesia in Katowice,
Katowice, Poland
*E-mail: kbednarczyk@us.edu.pl

Keywords: polymeric thin films, down feather, hydrophobic nanolayers, surface modification

Feathers and down feathers are one of the most biological and chemical complexed structures produced by living organisms. The extremely delicate biological structures are combined with exceptional lightness, strength and durability at changing temperatures. Feathers perform mainly isolating functions and are characterized by the largest weight to heat ratio of all known natural fibres, while maintaining their excellent elasticity. The investigations were focused on physico-chemical analysis of goose down feathers and goose down extracts with use a thin layer chromatography (TLC), a gas chromatography (GC), an infrared spectroscopy (FTIR), a thermogravimetric analysis (TGA), an energy dispersive X-ray spectroscopy performed in the scanning electron microscopy (EDX-SEM) and a scanning electron microscopy (SEM).

Further investigated properties inspired authors to prepare synthetic equivalents for such materials. The layer on down were produced using polyethers of branched architecture synthesised by controlled polymerization method. The polymers were diverse by molar mass, monomers and architecture of polymers whereas preparation of modified down were executed applying different method of activation of surface. Investigated layers were prepared by deep coating or speed coating methods. Prepared layers were characterized by spectroscopic, microscopic and thermogravimetric methods. The hydrophobic properties were analysed by contact angle as well as process of drench in long period. Obtained results were compared with natural feathers layers. The feathers were covered by polymer film from solutions of different concentration of macromolecules.

Thermochromic solar absorbers enhanced by nano-structuring

Anna Krammer[1*], *Tina Mitteramskogler*[2], *Andreas Schüler*[1]

[1]Solar Energy and Building Physics Laboratory, EPFL, Lausanne, Switzerland
[2]Functional Surfaces and Nanostructures, Profactor GmbH, Steyr-Gleink, Austria
[*]E-mail: anna.krammer@epfl.ch

Keywords: thermochromic, solar absorber, plasmonic absorber, nanoimprint lithography

Plasmonic absorbers have drawn increasing attention in many areas due to the wide range of surface nano-structuring methods available. Besides good selectivity, the appeal of plasmonic absorbers resides in the ease of tuning their optical properties by changing the geometry of the plasmonic structures.

An additive fabrication method combining UV nano-imprint lithography (UV-NIL) – for creating the nanopatterned mask, and magnetron sputtering – for the growth of metallic particles, has been proposed recently [1]. It promises a faster and cheaper approach for large area fabrication (roll-to-roll or roll-to-plate) of samples with high-resolution nanofeatures. The method consists of multiple steps: 1) spin-coating of the lift-off layer; 2) UV nanoimprint lithography; 3) reactive ion etching; 4) wet chemical development; 5) metal sputtering; 6) mask lift-off. This fabrication method has been successfully demonstrated for elliptical shaped W nanoparticles deposited on Si wafer [1].

In this work, we aim to combine the high absorptance of nanostructured, plasmonic absorbers with the temperature dependent thermal emissivity functionality of thermochromic absorbers. A thermochromic multilayered sample consisting of a Si substrate with a 135 nm W layer, to render the substrate IR reflective and stable at high deposition temperatures, a 35 nm SiO_2 interlayer, to help the adhesion between the thermochromic and W layer and a 350 nm thick thermochromic VO_2 film is selected for nano-structuring. Regularly placed, 200 nm wide and 110 nm high W nano-pillars have been deposited (Figure 1). Spectral reflectance curves of the new, plasmonic absorber reveal that surface nano-structuring increases the solar absorptance of the thermochromic sample by 8-9 percentage points, while a dynamic thermal emittance modulation, below and above the thermochromic transition temperature, is conserved.

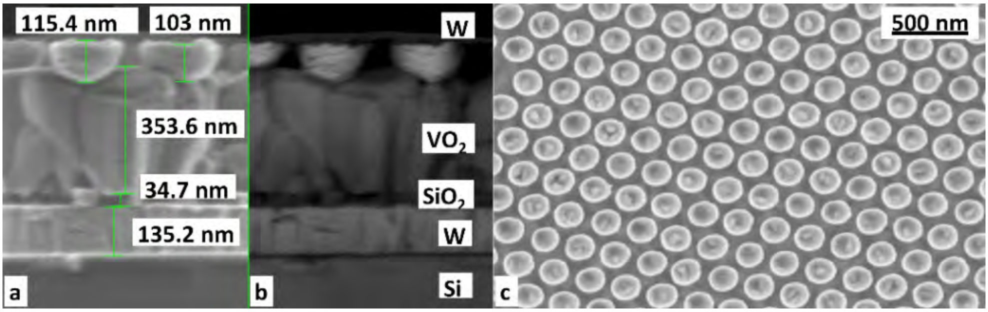

Figure 1. Secondary (a) and backscattered (b) electron image of the multilayer cross section with the corresponding layer thicknesses. Top-view SEM image of the 200 nm wide W nanoparticles (c).

Acknowledgments

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Detection of thin layers of multi-class pesticide residues with surface-enhanced Raman spectroscopy

Lara Mikac[1,2], Ema Kovačević[3], Šime Ukić[3], Matea Vrdoljak[1,2], Marijan Gotić[1,2], István Rigó[4], Miklós Veres[4], Mile Ivanda[1,2]*

[1]Center of Excellence for Advanced Materials and Sensing Devices, Ruđer Bošković Institute, Zagreb, Croatia
[2]Molecular Physics and New Materials Synthesis Laboratory, Ruđer Bošković Institute, Zagreb, Croatia
[3]Faculty of Chemical Engineering and Technology, Marulićev trg 19, Zagreb, Croatia
[4]Department of Applied and Nonlinear Optics, Institute for Solid State Physics and Optics, Wigner Research Centre for Physics, Budapest, Hungary
[*]E-mail: ivanda@irb.hr

Keywords: SERS, pesticides, substrate, silver, gold, colloid

The excessive use of pesticides disturbs the natural balance in the environment, creates resistance to pesticides and leads to water and food contamination [1]. Therefore, the implementation of fast, robust and cost effective techniques for the monitoring of pesticides is required. In this work surface-enhanced Raman spectroscopy (SERS) was used for the detection of four common pesticides atrazine, simazin, irgarol, and diuron. Sensitivity of the SERS method depends on the type of substrate that can be either a colloidal solution of metal nanoparticles (NPs) or a metal surface with a suitable nanostructured topology [2]. Here, the SERS substrates used for pesticides detection were silver and gold nanospheres as well as silver nanoprisms (Figure 1). Colloids with spherical NPs were produced by chemical reduction while Ag nanoprisms were prepared by reducing silver nitrate with borohydride (with citrate as a stabilizing agent) and stirring under a UV lamp for 10 h. The colloids were characterized by UV–Vis, DLS, zeta potential measurements, and SEM. The SERS results have shown that in the presence of synthesized NPs, it was possible to detect moderate to low concentrations of aforementioned pesticides. For example, under optimal experimental conditions, the detection limit of atrazine using Ag NPs was in the mM range whereas for simazine the estimated LOD was 50 μM.

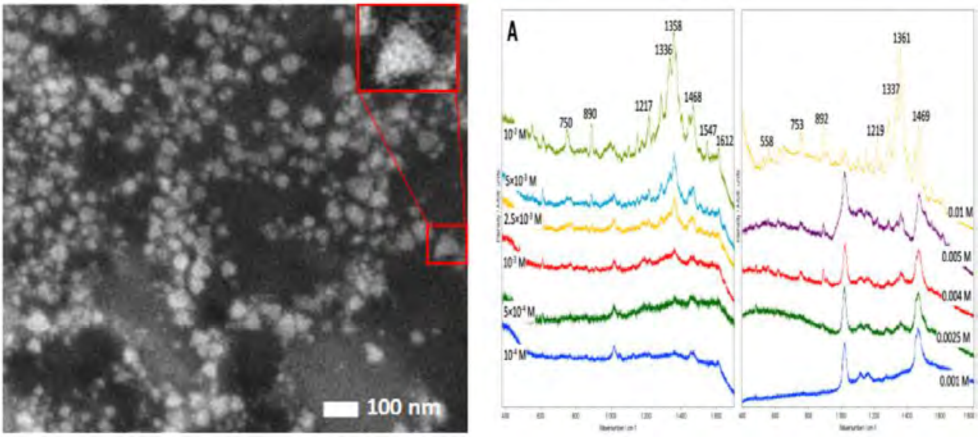

Figure 1. a) SEM image of Ag nanoprisms; b) SERS spectra obtained from different concentration of atrazine in methanol employing Ag nanospheres.

Acknowledgment

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Stitching of high resolution transmission electron microscope images for accurate measurement of distances

György Zoltán Radnóczi

Centre for Energy Research, Budapest, Hungary
E-mail: radnoczi.gyorgy.zoltan@energia.mta.hu

Keywords: HRTEM, calibration, epitaxy

The accuracy of the magnification values of a modern TEM is usually around 1-2% due to many variables that may be changed during alignment of the microscope. For carrying out more accurate measurements one needs to use calibration standards and make sure that imaging parameters match exactly for imaging the standard and the measured sample. Accuracy is improved if lattice fringes of known spacing appear in the measured image as an intrinsic standard, however this will limit the distances that can be measured to the frame size of the lattice resolution images. In a modern microscope this is usually less than 100 nm.

Measuring larger distances accurately may be carried out by recording several overlapping images and stitching them together. Stitching random images is commonly known, however, periodic lattices require artificial stitching marks (correspondence points) to avoid misalignment of images. In this work we used the electron beam of the transmission electron microscope to burn atomic scale dots on the sample. These dots were than used as correspondence points for very accurate alignment.

The use of this technique is demonstrated on a Si epitaxial layer viewed along the 110 zone axis. A layer thickness of about 1000 nm is measured with an accuracy of <0.5%. A detailed description of the process is provided, and its usability for accurately measuring large distances is discussed in detail.

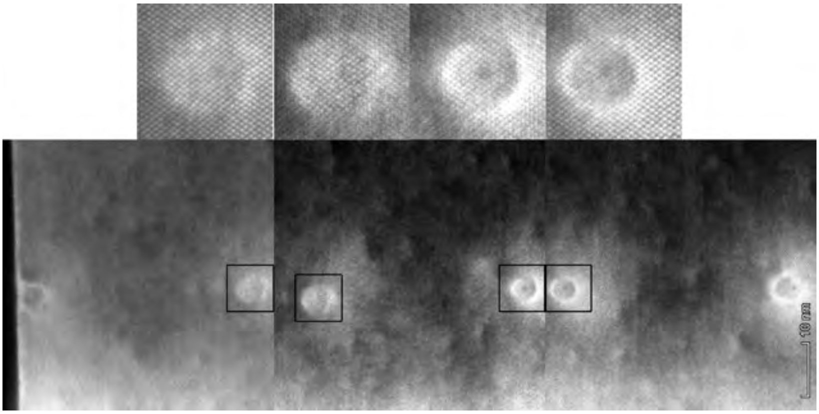

Figure 1. Stitching marks on neigboring HRTEM images used for aligning the overlapping images.

Acknowledgments

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Refractive index sensitivity of core-shell Ag@Au, Au@Ag nanoparticles

Géza Szántó[1*], *István Csarnovics*[1], *Attila Bonyár*[2]

[1]Department of Experimental Physics, University of Debrecen, Debrecen, Hungary
[2]Department of Electronics Technology, Budapest University of Technology and Economics, Budapest, Hungary
[*]E-mail: szanto.geza@gmail.com

Keywords: bulk refractive index sensitivity, localized surface plasmon resonance, LSPR, core-shell spheres, Ag@Au, Au@Ag

The bulk refractive index sensitivity of core-shell spherical bimetallic plasmonic nanostructures, namely Ag@Au and Au@Ag, were simulated with the MNPBEM MATLAB toolbox.

The inner radius of the nanoparticles (r_{core}) and the shell thickness (r_{shell}) were the running parameters. The range of the investigation was between 6nm and 45nm total radius ($r_{core}+r_{shell}$). The resolution of the internal radius and the layer thickness was 1nm. Boundary element method was used, and the surfaces of both the inner and the outer sphere were approximated by triangulation with 256 vertices.

The peaks appearing in the spectrum of the extinction cross-section were classified by wavelength. By changing the medium surrounding the nanoparticles between (water) n=1.33RIU and n=1.35RIU peak shift was observed and from it sensitivity was calculated. It was shown which r_{core} and r_{shell} sizes are beneficial when creating refractive index sensitive sensors.

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Intercalation of Au on hexagonal boron nitride monolayer prepared on Rh(111) and on gold coated Rh(111)

Gábor Vári[1], Richárd Gubó[2], János Kiss[3], Arnold Farkas,[3] László Óvári[2,3], András Berkó[3], Zoltán Kónya[1,3]*

[1]Department of Applied and Environmental Chemistry, University of Szeged, Szeged, Hungary
[2]Surface Dynamics Group, ELI Attosecond Light Pulse Source, Szeged, Hungary
[3]MTA-SZTE Reaction Kinetics and Surface Chemistry Research Group, Szeged, Hungary
*E-mail: ovari@chem.u-szeged.hu

Keywords: 2D nanomaterials, h-BN nanomesh, Au nanoparticles

Two dimensional monolayers (MLs) of hexagonal boron nitride (h-BN) are promising insulator components for nanoelectronics. The h-BN monolayer has a similar structure and lattice constant to those of graphene. On Rh(111) surfaces, monolayer h-BN forms a periodically corrugated structure, called “nanomesh” [1,2]. This feature is promising for its application as a nanotemplate.

Here we report on the growth of gold on the h-BN/Rh(111) and h-BN/Au-Rh/Rh(111) surfaces and on subsequent thermal effects studied by STM, XPS and low energy ion scattering (LEIS). The h-BN monolayer was formed on Rh(111) by the decomposition of borazine ($B_3N_3H_6$) at high temperatures (1000 K). Gold forms 1-2 atomic layer thick nearly 2D nanoparticles, when it is evaporated in small amounts (< 0,15 ML) on the nanomesh at 300 K. At higher coverages, the growth is definitively 3D. The gold peak was observed at a rather low position (83.7 eV), indicating significant electronic interaction with h-BN, as predicted by the previous density function theory (DFT) calculations [3]. The intercalation of gold is the dominant process upon stepwise thermal annealing to 1050 K, but agglomeration and evaporation also occur to a limited extent. Interestingly, the presence of ~ 0.15-0.6 ML of Au below the h-BN layer does not significantly influence the nanomesh structure. At higher gold doses a partial or full flattening of the nanomesh was observed [4].

We found significant changes in the intercalation process when we evaporated high amounts of gold (1-10 MLs) on h-BN/Rh(111) surface and subsequently annealed it. With increasing amounts of gold the Au LEIS intensity is also increasing but, during the annealing, the Au intensity decreases more steeply. We also studied Au intercalation on h-BN/Au-Rh/Rh(111) surfaces where the drop of Au intensities in LEIS was a somewhat slower than on h-BN/Rh(111) while the monolayer’s corrugation was present, however when the h-BN was prepared on 1.5 ML Au on Rh(111) the gold intensity decreased way more faster during the thermal impact. In XPS both N1s and B1s peak positions shifted down ~ 0.5 eV after the high amount of gold (5-10 MLs) intercalation.

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Study of clustering effect in magnetic nanoparticle based materials for biomedical applications

Vilmos Vékony[1*]*, Csaba Matta*[2]*, István A. Szabó*[1]

[1]Department of Solid State Physics, Faculty of Science and Technology, University of Debrecen,
Bem tér 18/b, Debrecen,H-4039, Hungary
[2]Department of Anatomy, Histology and Embryology, Faculty of Medicine, University of Debrecen,
Nagyerdei krt 98, Debrecen H-4032, Hungary
[*]E-mail: vekony.vilmos@science.unideb.hu

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Magnetic nanoparticles have several promising biomedical applications. One example is the magnetic nanoparticle based hyperthermia, where the magnetic nanoparticles absorbed by the tumor cells are subjected to alternating magnetic field to generate local heating. Other applications rely on the effect of static magnetic fields to collect or rearrange cells, which are covered with magnetic nanoparticle containing substrates. In both cases, the effect of clustering largely modifies the magnetic properties of these materials.

In the present study, we have examined a multicomponent material, NanoShuttle™-PL (Greiner Bio-One) particles composed of gold, iron oxide and poly-L-lysine, which are used for the creation of levitated 3D cell cultures. The aim of the study was to understand the structure of this composite material for the characterisation of the clustering of the magnetic nanoparticles, which is frozen in the matrix material (see Figure 1).

We have performed RAMAN, AFM/MFM measurements and TEM investigation of the composite material deposited on a substrate. Magnetic properties were investigated with a vibrating sample magnetometer (VSM) both in the liquid state and in the surface extracted form.

Based on the identified structural features we are developing a simulation model for the determination of magnetic properties of the clusters in order to simulate the effect of external static and alternating magnetic field on these particles.

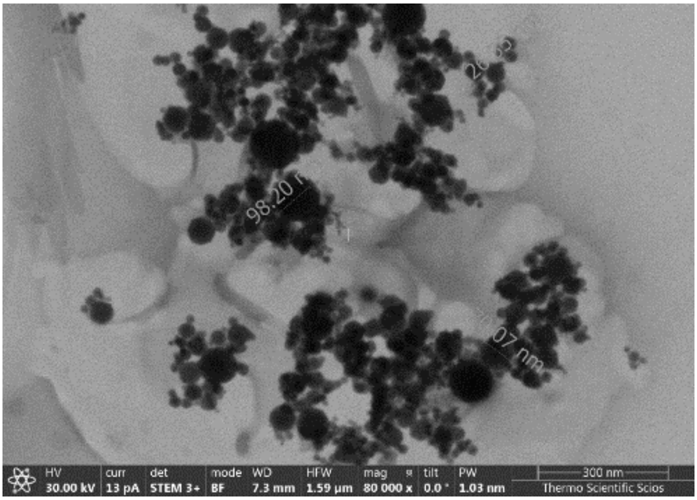

Figure 1: TEM image of the magnetite particles embed in a gold matrix.

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