Foreward

Nanophysics and solar energy conversion are priorities for modern physics, due to the rapid developments of atomic scale devices and to the vital need of valorizing renewable energy resources. They are essentially domains of interdisciplinary research, where applied, computational and theoretical physics, as well as chemistry and electrochemistry must all contribute.

In such a field, rapid exchange of information, of ideas, of bibliographical resources, of experimental approaches is essential for the progress of knowledge. The workshop will put together researchers who investigate several important directions in nanophysics and solar energy conversion – experimental, theoretical and computational physicists, chemists and engineers, constituting an excellent oportunity of exchange of ideas, dissemination of research and preparation of scientific projects.

The workshop is the third one, organized in Magurele on this theme, mainly by the National Institute of Material Physics, the Physics Department of the University of Bucharest, the UNESCO Chair at Horia Hulubei Foundation, and ICTP. The Romanian partners are grateful to ICTP for the financial support constantly received, which was vital for the existence of these scientific events.

Victor Barsan
Scientific Secretary of the workshop
UNESCO Chair at Horia Hulubei Foundation
& National Institute for Physics and Nuclear Engineering

Lecturers

Stefan ANTOHE (*University of Bucharest, Physics Department, santohe@solid.fizica.unibuc.ro*): Photovoltaic cells based on A2-B6 semiconducting compound for space applications

Petre BADICA (*INFM, Bucharest, badica2003@yahoo.com*): MgB_2-based composites obtained by spark plasma sintering for superconductivity and biomedical applications

Dan BATALU (*Politechnica University, Bucharest, dan_batalu@yahoo.co*): Search for materials with potential for medical applications

Anca BIRSAN (*INFM, Bucharest, anca_birsan@infim.ro*): Tunning magnetism in full-Heusler compounds

Tiberius CHECHE (*University of Bucharest, Physics Department, tiberiuscheche@yahoo.com*): Strain influence on optical absorption of giant semiconductor colloidal quantum dots

Fanica CIMPOESU (*Institute for Physical Chemistry, Bucharest, fanica.cimpoesu@yahoo.com*): Ab initio calculations and ligand field modeling as tools for understanding and predicting magnetic and optical properties of d and f metal ion systems

Raluca CONSTANTINEANU (*University of Bucharest, Physics Department, neanu68@yahoo.com*): Spectral response of photovoltaic cells based on CdS/CdTe heterojunction with different TCO's

Daniela DRAGOMAN (*University of Bucharest, Physics Department, danieladragoman@yahoo.com*): Perspectives on carbon electronics

Pavo DUBCEK (*Boskovic Institute, Zagreb, Pavo.Dubcek@irb.hr*): Applications of the grazing incidence small-angle X-ray spectroscopy (GISAXS)

Paul GARTNER (*INFM, Bucharest, gartner@infim.ro*): A scaling-limit approach to the laser transition

Mihai GIRTU (*Ovidius University, Constanta, mihai.girtu@univ-ovidius.ro*): New Co(II) complexes as electrolytes for dye-sensitezed solar cells. Electron transfer, dye regeneration and control of the open-circuit voltage

Eric Daniel GLOWACKI (*LIOS, Linz, eric_daniel.glowacki@jku.at*): Electronic materials inspired by nature - progress in bioelectronics

Andrea GOLDONI (*Elettra Synchrotron Facility, andrea.goldoni@elettra.eu*): Nanotechnology and synchrotron radiation for solar cell materials

Gabriela IACOBESCU (*University of Craiova, gabrielaiacobescu@yahoo.com*): Laser influence on multilayer Ag/Ni and Ag/Ce magnetic thin film structures prepared by thermionic vacuum arc technology

Sorina IFTIMIE (*University of Bucharest, Physics Department, sorinaiftimie@yahoo.com*): Physical properties of different metallic oxide thin films prepared by direct thermal oxidation

Victor KUNCSER (*INFM, Bucharest, kuncser@infim.ro*): Magnetic nanostructures and bio-medical applications

Lucia LEONAT (*LIOS, Linz, lucialeonat@gmail.com*): Solar cells on paper substrate

Michael LIEBRECHT (*Johannes Kepler University, Linz, michael.liebrecht@jku.at*): Van der Waals interaction in density functional theory

Vanni LUGHI (*University of Trieste, vlughi@units.it*): Nanotechnology for photovoltaics

Corneliu Florin MICLEA (*INFM, Bucharest, miclea@infim.ro*): Unconventional vortex pinning in non-centrosymmetric superconductors

Adela NICOLAEV (*University of Bucharest, Physics Department, adela_nicolaev@yahoo.com*): Transport in ferrocene single molecules for terahertz applications

Nenad NOVKOVSKI (*Skopje University, Physics Department, nenad@novkovski.com*): Method of successive extraction of various contributions in absorption spectra of solids

Branko PIVAC (*Boskovic Institute, Zagreb, pivac@irb.hr*): Solar cells based on quantum structures

Nicola SERIANI (*ICTP, nseriani@ictp.it*): Ab-initio investigation of Cu@TiO_2 photocatalysts

Aleksandar SKEPAROVSKI (*Skopje University, Physics Department, skepalek@gmail.com*): Breakdown and wearout phenomena in high-k dielectrics

Stefan STANCIU (*University of Bucharest, Physics Department, stanciu_stefan2008@yahoo.com*): The asymmetric well: a way to understanding core-shell quantum dots

Radostyna STOYANOVA: (*Institute of Chemistry, Sofia, radstoy@svr.igic.bas.bg*): Nano approach to more effective electrode materials for Lithium and Sodium ion batteries

Mugurel TOLEA (*INFM, Bucharest, tzolea123@yahoo.com*): Electrons in 2D isospectral shapes: phase extraction and few-particles properties

Marco TRUCCATO (*University of Torino, marco.truccato@unito.it*): Single crystal superconducting oxides: from precursors to devices. Is a novel X-ray lithography possible?

Ellie UZUNOVA (*Institute of Chemistry, Sofia, ellie.uzunova@gmail.com*): Adsorption and photoactivation of probe molecules on transition metal oxide nanoclusters and molecular complexes. Reaction mechanism of conversion to fuel.

Richard WOLLHOFEN (*Johannes Kepler University, Linz, Richard.Wollhofen@jku.at*): Nano-confined polymer structures for adhesive protein binding

Marian ZAMFIRESCU (*INFLPR, Magurele-Bucharest, marian.zamfirescu@inflpr.ro*): Large area surface nanopatterning by ultrafast laser pulses

Programme

Monday, September 1, 2014

9.30 - 9.35: Opening talks: Ionut Enculescu, Nicola Seriani, Stefan Antohe

Session 1: Photovoltaics (1); chairperson: Nicola Seriani

9.35 - 10.05: Andrea GOLDONI (Elettra Synchrotron Facility): Nanotechnology and Synchrotron Radiation for Solar Cell Materials

10.05 - 10.35: Radostyna STOYANOVA: (Institute of Chemistry, Sofia): Nano Approach to more effective electrode materials for Lithium and Sodium Ion Batteries

10.35 - 11.05: Stefan ANTOHE (University of Bucharest, Physics Department): Photovoltaic cells based on A2-B6 semiconducting compound for space applications

11.05 - 11.20: Coffee break

Session 2: Photovoltaics (2); chairperson: Eric Daniel Glowacki

11.20 - 11.50: Tiberius CHECHE (University of Bucharest, Physics Department): Strain Influence on Optical Absorption of Giant Semiconductor Colloidal Quantum Dots

11.50 - 12.05: Sorina IFTIMIE (University of Bucharest, Physics Department): Physical properties of different metallic oxide thin films prepared by direct thermal oxidation

12.05 - 12.20: Raluca CONSTANTINEANU: Spectral response of photovoltaic cells based on CdS/CdTe heterojunction with different TCO's

12.20 - 12.50: Nicola SERIANI (ICTP): Ab-initio investigation of Cu@TiO_2 photocatalysts

12.50 - 13.20: Mihai GIRTU (Ovidius University, Constanta): New Co(II) complexes as electrolytes for dye-sensitezed solar cells. Electron transfer, dye regeneration and control of the open-circuit voltage.

13.20 - 14.30: Lunch

Session 3: Special topics of materials physics; chairperson: Radostina Stoyanova

14.30 - 15.00: Pavo DUBCEK (Boskovic Institute, Zagreb): Applications of the grazing incidence small-angle X-ray spectroscopy (GISAXS)

15.00 - 15.30: Aleksandar SKEPAROVSKI (Skopje University, Physics Department): Breakdown and wearout phenomena in high-k dielectrics

15.30 - 16.10: Nenad NOVKOVSKI (Skopje University, Physics Department): Method of successive extraction of various contributions in absorption spectra of solids

16.10 - 16.25: Coffee break

Session 4: Optics and photonics; chairperson: Nenad Novkovski

16.25 - 16.55: Gabriela IACOBESCU (University of Craiova): Laser influence on multilayer Ag/Ni and Ag/Ce magnetic thin film structures prepared by Thermionic Vacuum Arc technology

16.55 - 17.25: Marian ZAMFIRESCU (INFLPR, Magurele-Bucharest): Large area surface nanopatterning by ultrafast laser pulses

19.00: Welcome Party (Academia House / Casa Universitarilor)

Tuesday, September 2, 2014

Session 5: Superconductivity at nanoscale; chairperson: Victor Kuncser

9.30 - 10.00: Petre BADICA (INFM, Bucharest): MgB2-based composites obtained by Spark Plasma Sintering for superconductivity and biomedical applications

10.00 - 10.30: Dan BATALU (Politechnica University, Bucharest): Search for materials with potential for medical applications

10.30 - 11.00: Marco TRUCCATO (University of Torino, Italy): Single crystal superconducting oxides: from precursors to devices. Is a novel X-ray lithography possible?

11.00 - 11.15: Coffee break

Session bis2: Photovoltaics; chairperson: Vanni Lughi

11.15 - 11.55: Eric Daniel GLOWACKI (LIOS, Linz): Electronic materials inspired by nature -progress in bioelectronics

Session 6: The youngest physicists session; chairperson: Vanni Lughi

11.55 - 12.05: Michael LIEBRECHT , Richard WOLLHOFEN (Johannes Kepler University, Linz): Short presentation of the Wilhelm Macke Foundation

12.05 - 12.25: Michael LIEBRECHT (Johannes Kepler University, Linz): Van der Waals interaction in Density Functional Theory

12.25 - 12.45: Richard WOLLHOFEN (Johannes Kepler University, Linz): Nano-Confined Polymer Structures for Adhesive Protein Binding

12.45 - 13.00: Adela NICOLAEV (University of Bucharest, Physics Department): Transport in ferrocene single molecules for terahertz applications

13.00 - 13.15: Stefan STANCIU (University of Bucharest, Physics Department): The asymmetric well: a way to understanding core-shell quantum dots

13.15 - 14.30: Lunch

Session 7: Materials physics for renewable energy; chairperson: Fanica Cimpoesu

14.30 - 15.00: Vanni LUGHI (University of Trieste): Nanotechnology for Photovoltaics

15.00 - 15.30: Branko PIVAC (Boskovic Institute, Zagreb): Solar cells based on quantum structures

15.30 - 16.00: Lucia LEONAT (LIOS, Linz): Solar cells on paper substrate

16.00 - 16.15: Coffee breack

Session 8: Computational approach to materials physics; chairperson: Aleksandar Skeparovski

16.15 - 16.45: Ellie UZUNOVA (Institute of Chemistry, Sofia): Adsorption and photoactivation of probe molecules on transition metal oxide nanoclusters and molecular complexes. Reaction mechanism of conversion to fuel.

16.45 - 17.15: Fanica CIMPOESU (Institute for Physical Chemistry, Bucharest): Ab initio calculations and Ligand Field modeling as tools for understanding and predicting magnetic and optical properties of d and f metal ion systems

17.15 - 18.15: Round table: New opportunities in materials research in NIMP: launching RITECC - Research Innovation &Technology Centre - a project financed through POS CCE programme; chairperson: Ionut Enculescu, General Director of INFM - Magurele-Bucharest

Wedenesday, September 3, 2014

Session 9: Nanophysics; chairperson: Ellie Uzunova

9.30 - 10.10: Victor KUNCSER (INFM, Bucharest): Magnetic nanostructures and bio-medical applications

10.10 - 10.40: Anca BIRSAN (INFM, Bucharest): Tunning magnetism in full-Heusler compounds

10.40 - 11.10: Corneliu Florin MICLEA (INFM, Bucharest): Unconventional vortex pinning in non-centrosymmetric superconductors

11.10 - 11.25: Coffee break

Session 10: Theoretical aspects of solid state physics; chairperson: Nicola Seriani

11.25 - 11.55: Mugurel TOLEA (INFM, Bucharest): Electrons in 2D isospectral shapes: phase extraction and few-particles properties

11.55 - 12.25: Paul GARTNER (INFM, Bucharest): A scaling-limit approach to the laser transition

12.25 - 13.05: Daniela DRAGOMAN (University of Bucharest, Physics Department): Perspectives on carbon electronics

13.05 - 13.15: Workshop closure; final remarks

13.15 - 14.30: Lunch

Photovoltaic cells based on A2-B6 semiconducting compound for space applications

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Due to their physical and chemical properties (such as suitable band gaps, large absorption coefficients and good chemical stability) CdS and CdTe thin films are interesting materials for electronic and optoelectronic devices, including particularly, the photovoltaic cells for both terrestrial and space applications. For this specific application, it is of prime importance to study the influence of ionizing radiations on the structural, electrical and optical properties of the component materials on a hand and on the photovoltaic structures based on them, on the other hand.

In this paper, the photovoltaic cells based on CdS/CdTe thin films, produced by thermal vacuum sublimation, were irradiated with protons and alpha particles, (both components of cosmic rays), at room temperature. The irradiation energy for both protons and alpha particles was 3 MeV and the fluencies were 10^{14} protons/cm^2 and 10^{13} alpha particles/cm^2, respectively. The prepared samples configuration was a "superstrat" one having CdS as "window" layer and CdTe as "absorber" layer, respectively. The films were deposited by conventional thermal vacuum evaporation technique. The CdS/CdTe is given a post deposition $CdCl_2$ heat treatment which enables grain enhancement, reduces the defect density in the films, promotes the interdiffusion of the CdTe and CdS layers and thereby improves solar cell efficiency. The effects of irradiation were studied by investigating the changes in the electrical and optical properties of the cells. The structures were electrical characterized before and after protons and alpha particles irradiation by measuring the I-V characteristics both in dark and in AM 1.5 conditions and the results were compared. The parameters characterizing a photovoltaic cell, short-circuit current, open circuit photovoltage and fill factor were calculated before and after protons and alpha particles irradiation and the obtained values are comparable, but less for irradiated samples. Moreover, the maximum power obtained for a photovoltaic cell half decreased after alpha particles irradiation. A discussion about the possible origin of those defects is given. In this sense, it was found that proton irradiation in the above mentioned conditions results mainly in the introduction of defects at the CdS/CdTe interface.

Keywords: Solar cells, Cadmium Telluride, Thin Films, Proton and Alpha Particles Irradiation

MgB_2-based composites obtained by Spark Plasma Sintering for superconductivity and biomedical applications

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MgB_2 as a superconductor is intensively studied worldwide. This because MgB_2 has a high potential for different applications. MgB_2 is a light-weight material, it is a simple compound made of two elements with a hexagonal layered crystal structure, it is available, it has a low price, it is relatively stable under normal conditions, it has a relatively high critical temperature Tc of about 39K, and it has interesting physics.

To improve the functional characteristics of MgB_2 such as critical current density Jc and irreversibility field Hirr, additives can be used. Literature indicates that additives can contribute to flux pinning and further to the Jc-increase through chemical substitution effects that generate local disorder into MgB_2 crystal lattice. Popular is substitution of B by C supplied from different source materials such as e.g. SiC [1]. Pinning can be also enhanced through 'composite' effects. In this approach, impurities at nano scale comparable to coherence length of MgB_2 (about 20 nm) or interfaces between the impurity and the superconductor are embedded in the MgB_2 matrix. Interfaces can be viewed as grain boundaries and in MgB_2 the problem of weak links specific for high temperature superconductors is not a critical issue. In fact, it is remarkable that grain boundaries are efficient pinning centers in MgB_2 [2]. This situation suggests the necessity of nanostructuring of MgB_2 in a way that leads to introduction of more and modified grain boundaries and interfaces. Not only additives can play a significant role in this direction, but also the processing technology applied to obtain the MgB_2-based composite is important. Search of new effective additives and technologies for the functional characteristics enhancement in MgB_2 is among the priorities in the field of applied superconductivity.

Bulk dense samples were obtained by Spark Plasma Sintering (SPS) applied on mixtures of MgB_2 and additive powders. Additives were Sb_2O_3, Bi_2O_3, TeO_2, Te, SiC, (SiC+Te), RE_2O_3 (RE = Ho, La, Eu), GeO_2, Ge, $Ge_2C_6H_{10}O_7$ and cubic BN. These additives are shown to enhance Jc and Hirr. We shall discuss different aspects of structure, microstructure and vortex pinning in our composite samples.

We have also tested MgB_2-based materials added with Eu_2O_3 as a potential candidate for biomedical applications. Measurements of Vickers hardness, pH evolution in the phosphate-buffered saline solutions, corrosion resistance (Tafel polarization curves), cytotoxicity (in vitro tests) and antibacterial activity will be presented.

[1] Dou SX, Soltanian S, Horvat J, Wang XL, Zhou SH, Ionescu M, Liu HK, Munroe P, Tomsic M, Enhancement of the critical current density and flux pinning

of MgB_2 superconductor by nanoparticle SiC doping, Appl. Phys. Lett. **81** (2002) 3419-3421.
[2] Larbalestier DC, Cooley LD, Rikel MO, Polyanskii AA, Jiang J, Patnaik S, Cai XY, Feldmann DM, Gurevich A, Squitieri AA, Naus MT, Eom CB, Hellstrom EE, Cava RJ, Regan KA, Rogado N, Hayward MA, He T, Slusky JS, Khalifah P, Inumaru K, Haas M, Strongly linked current flow in polycrystalline forms of the superconductor MgB_2, Nature **410** (2001) 186-189.

Search for materials with potential for medical applications

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Search of materials for medical applications is of high interest. These materials and their technologies often require unconventional approaches. In contact with human body, side effects usually occur. The intensity of the side effects is related to the devices' or patient's individuality. For example in the case of stents the causes can be due to the metallic material used for manufacturing the device, the coating materials (oxides, polymers etc) or even the medicine itself. In order to obtain a "zero" side effect, current research efforts are concentrated on new materials, implant's design, drugs and procedures to decrease the rate of negative results [1-3].

Liu *et al.* showed that NiTi alloy coated with TiO_2 film has improved blood compatibility [1]. Xi *et al.* investigated the degradation behavior of a poly(lactic acidco-glycolic acid) coating on cobalt-chromium stent platform [4]. Studies were also made for the replacement of permanent metallic stents with fully biodegradable stents [5, 6]. Xu *et al.* studied the biodegradation behavior of PLGA stents both *in vitro* and *in vivo*

to explore the usefulness of biodegradable polymeric stents in human common bile duct (CBD) repair and reconstruction [7].

In our work, we use TiNi shape memory alloy as substrate on which subsequent sandwich layers are deposited. Coatings consisted of oxides, XO_2 (X=Si, Zr and Ti), or of the same oxides covered atop by a polymer (poly lactide-co-glycolide), (DL (PLG) - $[C_3H_4O_2]_x[C_2H_2O_2]_y$). XO_2 coatings are designed to block the undesired Ni diffusion into tissue for minimizing its harmful side effects. Ni is well established as an allergen, toxic and carcinogen element. The polymeric layer was designed to be a drug deliverer. Stents of TiNi with oxide or composite coatings were implanted in rabbits. Coatings features vs. their implantation effects are presented and discussed.

On the other hand, a new approach of biodegradable biomaterials is considered, using not polymers, but various alloys e.g. based on Fe or Mg. Recent studies [8-12] show the importance of magnesium based materials [9], due to their low density, good initial mechanical properties (close to those of the bones) and biodegradability. The last aspect is very important, when we consider the surgical reasons [13, 14]. At the same time, there are some negative issues such as corrosion rate being still high. The consequence is a fast decrease of the mechanical properties of the implant before the newly formed bone can sustain the necessary mechanical load. Another issue is the hydrogen release (as a reaction product, 1 liter per 1 g of Mg), and pH values of solution, up to 11 for pure Mg.

In our work we studied the hardness, pH evolution in PBS, corrosion resistance, cytotoxicity, antibacterial behaviour, and structural characteristics of pristine and Eu_2O_3-added MgB_2. Results suggest that MgB_2 based composites usually priced for superconductivity could also have potential for biomedical applications such as biodegradable implants and sterile instruments.

References

[1] J.X. Liu, D.Z. Yang, F. Shi, Y.J. Cai, (2003), Sol–gel deposited TiO_2 film on NiTi surgical alloy for biocompatibility improvement, Thin Solid Films, 429(1-2), 225-230

[2] U. Westedt, M. Wittmar, M. Hellwig, P. Hanefeld, A. Greiner, A.K. Schaper, T. Kissel (2006), Paclitaxel releasing films consisting of poly(vinyl alcohol)-graft-poly(lactide-co-glycolide) and their potential as biodegradable stent coatings, Journal Control. Release, 111, 235–246

[3] X. Wang, S.S. Venkatraman_, F.Y.C. Boey, J.S.C. Loo, L.P. Tan, (2006), Controlled release of sirolimus from a multilayered PLGA stent matrix, Biomaterials, 27, 5588–5595.

[4] T. Xi, R. Gao, B. Xu, L. Chen, T. Luo, J. Liu, Y. Wei, S. Zhong, (2010), In vitro and in vivo changes to PLGA/sirolimus coating on drug eluting stents, Biomaterials, 31, 5151-5158

[5] S.S. Venkatraman, L.P. Tan, J.F.D. Joso, F. Boey, X.T. Wang, (2006), Biodegradable stents with elastic memory, Biomaterials 27, 1573–1578.

[6] S. Venkatraman, L.P. Tan, T. Vinalia, K.H. Mak, F. Boey (2003),Collapse pressures of biodegradable stents. Biomaterials, 24, 2105–2111.

[7] X. Xu, T. Liu, K. Zhang, S. Liu, Z. Shen, Y. Li, X. Jing, (2008), Biodegradation of poly(L-lactide-co-glycolide) tube stents in bile, Polym. Degrad. Stab., 93, 811-817.
[8] F. Witte, V. Kaese, H. Haferkamp, E. Switzer, A. Meyer-Lindenberg, C.J. Wirth, H. Windhagen, In vivo corrosion of four magnesium alloys and the associated bone response, Biomaterials 26 (2005) 3557-3563.
[9] M.P. Staiger, A.M. Pietak, J. Huadmai, G. Dias, Magnesium and its alloys as orthopedic biomaterials: A review, Biomaterials 27(2006) 1728-1734.
[10] F. Witte, J. Fischer, J. Nellesen, H.A. Crostack, V. Kaese, A. Pisch, F. Beckmann, H. Windhagen, In vitro and in vivo corrosion measurements of magnesium alloys, Biomaterials 27 (2006) 1013-1018.
[11] Z. Shi, G. Song, A. Atrens, The corrosion performance of anodised magnesium alloys, Corros. Sci., 48 (2006) 3531-3546.
[12] G. Song, Control of biodegradation of biocompatible magnesium alloys, Corros. Sci. 49 (2007) 1696-1701.
[13] G.O. Hofmann, Biodegradable implants in traumatology: a review on the state-of-the-art, Arch. Orthop. Traum. Su. 114 (1995) 123-132.
[14] L. Claes, A. Ignatius, Entwicklung neuer biodegradabler Implantate, Der Chirurg 73 (2002) 990-996.

Tuning magnetism in full-Heusler compounds

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Ti-based Heusler compounds [1] with X_2YZ stoichiometric formula represent a new class of ternary intermetallics susceptible to revolutionary applications in spintronics. Some of these compounds behave like semiconductors for one spin direction and like metal for the other spin direction and therefore present half-metallic properties [2] and potential 100% spin polarization at the Fermi level. The breakdown of the half-metallic state is related to the transition from ferri- to ferromagnetism by quenching the magnetic moment orientation of Y element regarding the one of X element.

Within the framework of Density Functional Theory, studies on Ti_2FeSn [3] and Ti_2CoSn [4] full-Heusler compounds were performed. The electronic structures investigated by first principle calculations are theoretically discussed and a parallel is drawn between the magnetic properties obtained on bulk structures.

References:

[1] Fr. Heusler, Verh. Deutsch. Phys. Ges. 5 (1903) 219.

[2] R.A. de Groot, F.M. Mueller, G. van Engen, K.H.J. Buschow, Phys. Rev. Lett. 50 (1983) 2024.
[3] A. Birsan, P. Palade Intermetallics 36 (2013) 86.
[4] A. Birsan, P. Palade, V. Kuncser, Solid State Commun. 152 (2012) 2147.

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Strain Influence on Optical Absorption of Giant Semiconductor Colloidal Quantum Dots

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The strain field of core/multishell structures with spherical symmetry is modeled by a linear continuum elasticity approach. The effect of the lattice mismatch strain on the energy structure and linear optical absorption in thick core/shell/shell spherical semiconductor quantum dots is analyzed within the strain model we propose. The predicted fundamental excitonic absorption of CdSe/CdS/ZnS and ZnTe/ZnSe/ZnS 'giant' core/shell/shell spherical quantum dots is compared against the experimental data. Localization of the photoexcited carriers induced by coating is found to play an important role in explaining the optical stability of large core/shell/shell spherical quantum dots.

Prospecting the properties of lanthanide-based systems with new modeling methodologies

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Lanthanides represent an interesting area of the periodic table, the compounds made with such ions (oxides, salts, coordination complexes) showing properties attractive for new applications and technologies.[i] Particularly, in the last few years was recorded a boom in the quest for systems behaving as magnets at molecular and nano-scale levels, based on intrinsic magnetic anisotropy of the f-type ions.[ii] At the same time, this topic is challenging in fundamental respects, being related with particular electronic structure features of the lanthanide ions in molecules, e. g. non-*aufbau* occupation schemes. Due to such hidden problems, for long time the modern *ab initio* methods were not applied to lanthanide compounds, in sharp contrast to the treatment of systems with d-type transition ions, which were frequently accounted by computation modeling, complementary to the experimental accounts. We claim pioneering breakthroughs in this field, performing the first multi-configuration *ab initio* calculations on lanthanide complexes by an innovative methodology based on fragment-merged starting orbitals.[iii] At the same time, we designed powerful tools in accounting the magnetic anisotropy.[iv] Such advances were possible by close cooperation with experimental peoples, aiming to understand all the sides of the data landscape.

Since, from modeling point of view, the treatment of molecular magnetism implies, in general, the same tools as required for the account of other properties, we recently turned our interest in optical manifestations, aiming for structure-property correlations in this field. We conduct our approach at the borderline of state-of-the art quantum calculations and phenomenological modeling (by Ligand Field Theory), in confluence with the experimental data. Thus, we approached[v] the engineering of 4f-5d transitions in systems used in new types of LED-based light bulbs, aiming to tune a spectrum similar to the solar one, the so-called warm-white-light, curing the non-natural bluish tone of current devices. In principle, on long run, we aim extending our deals to other properties based on lanthanide or actinide f-f or d-f transitions, e.g. with relevance in laser technologies, considering that the theoretical approach is a powerful complement to the experiment, enlightening the way to the design of special properties, by understanding the causal determinations.

Spectral response of photovoltaic cells based on CdS/CdTe heterojunction with different TCO's

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Photovoltaic cells based on cadmium telluride (CdTe) were prepared by thermal vacuum evaporation (TVE) technique onto optical glass substrates covered with ITO or ITO/IGZO as transparent conductive oxides (TCO's). Indium gallium zinc oxide (IGZO) thin films were deposited in situ onto indium tin oxides layers (ITO), by magnetron sputtering. Optical investigations were made for both, the transparent conductive oxide layers and photovoltaic cells component films, using a Perkin Elmer spectrometer. The optical transmittance spectra were drawn at room temperature in the 190 – 1100 nm and the obtained values were higher than 60% for all transparent oxide layers. From absorption spectra of cadmium sulfide (CdS) and CdTe the optical gap values were determined and were similar with those from literature. The morphological analyses of the prepared photovoltaic cell's surface were performed by scanning electron microscopy (SEM) and the structural features for cadmium sulfide and cadmium telluride thin films were determined by X-ray measurements. A well-defined crystalline structure was observed for both CdS and CdTe layers. The external quantum efficiency (EQE) values were determined for the prepared PV cells, at room temperature.

The obtained experimental data proved that IGZO thin film can be used as TCO's replacing ITO; moreover, a photoelectrical behavior was revealed improving the photovoltaic performances of the prepared samples.

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Perspectives on carbon nanoelectronics

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The talk is focused on state-of-the-art nanoelectronic devices based on carbon nanotubes and graphene, and on the issues that need to be solved in the near future in order to fully exploit the potentialities of these materials. The talk starts with a brief introduction to the transport properties of charge carriers in these carbon-based materials, with the aim of emphasizing the differences with respect to other semiconductor materials used in nanoelectronics. These differences, brought about by the massless Dirac-like equation satisfied by charge carriers in graphene, cause unique phenomena such as ambipolar conduction, Klein paradox and the finite minimum conductivity in graphene, and explain the conduction properties of semiconducting or metallic carbon nanotubes.

The second part of the talk exemplifies the gap between theoretical predictions and actual performances attained by common devices, such as field-effect transistors based on graphene, and highlights the issues that need to be solved in order to understand charge carrier transport in these devices, and thus improve the modeling of graphene-based devices. Apart from the need to investigate thoroughly the limitations of common graphene-based devices, another avenue that could be exploited for future carbon electronics is to develop devices based on the distinctive characteristics of carbon nanotubes and graphene. Such devices should work in the ballistic regime and should use new configurations for achieving known functionalities. Some examples in this respect are given.

Thin film probing from small angle

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Small Angle X-ray scattering (SAXS) has been extensively used on size and shape investigation of nanometer size inhomogeneities in different fields, ranging from biophysics, where it originated, to materials science. The advance of thin films research, with thickness and structural details in nanometer range, resulted in intensive SAXS application, albeit in the grazing incidence set up (GISAXS).

The sensitivity of GISAXS on the surface roughness is employed in the investigation of the quality of a homogeneous film growth, and the thickness and the density of the film are determined precisely. Density variation versus thickness and/or interdiffusion between two films can be evaluated. The size and shape of the

nanostructures (in form of particles or vacancies, precipitations or agglomerations) that are present in the film can be precisely determined, as well as their depth distribution. The presence of nanoparticles on the film surface, or on the interface between different films in form of islands is clearly resolved.

On the other hand, organized and self organized nanostructures investigation bridges the gap between SAXS as diffuse scattering and crystallography. Repetitive bilayer structure, with repeating motif thickness of few nanometers, gives rise to peaked X-Ray reflectivity at small angles, not unlike a diffraction curve found in a typical textbook on powder diffraction. In addition, combination of selected film materials and thicknesses of the individual layers, together with post deposition annealing, results in nanoparticle formation in one of the bilayers that are self organized. This kind of structures are investigated in a crystallographic manner, only the angular range is reduced to few degrees, and size shape of particles has to be accounted for. Furthermore, dynamics of islands formation on substrate surface can also lead to self organization, and this results in a structure which has two dimensional crystal properties.

A scaling-limit approach to the laser transition

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A two-level emitter interacting with a cavity photon mode is the simplest instance of cavity quantum electrodynamics. Despite its simplicity it shows a nontrivial behaviour and undergoes a drastic regime change at the lasing transition. The similarity to a phase transition has been pointed out in the literature. The change is seen in the pump dependence of the steady-state exciton and photon populations. As in the phase-transition case, it is expected that a sharp transition is made possible only by a certain limiting procedure. By solving analytically the steady-state problem it is shown that the appropriate limit involves the vanishing of the rate of cavity losses, $\kappa \to 0$, and vanishing of the light-matter coupling, $g \to 0$, so that g^2/κ stays finite and $g^2/\kappa > 2\gamma$, where γ is the rate of nonradiative excitonic losses. Lasing is diagnosed by checking that the photon statistics becomes purely Poissonian. The above limiting procedure is also tested on a different laser model, namely the Scully-Lamb random injection process.

New Co(II) complexes as electrolytes for dye-sensitezed solar cells. Electron transfer, dye regeneration and control of the open-circuit voltage.

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We report the results of a combined experimental and theoretical study with the aim to control the open circuit voltage and increase the overall photovoltaic conversion efficiency of the device by varying the redox level of the electrolyte. We synthesized and studied a new series of mixed ligand Co(II) complexes, $[Co(AA)(BB)_2]X_2$, where AA and BB are derivatives of 1,10-phenanthroline and 2,2'-bipyridil, X=Cl^-, $TFSI^-$ (TFSI= bis(trifluoromethanesulfonyl)imide), as redox electrolytes for dye-sensitized solar cells (DSSC). Compared to the I_3^-/I^- system, the cobalt(III/II) polypyridyl complex redox shuttles have low visible light absorption, and the ease of tuning their redox potentials is a very significant aspect for accomplishing a photovoltage enhancement.

The synthetic strategy of such heteroleptic compounds is a challenge due to the tendency of the Co(II) ion to form tris chelates compounds or to disproportionate. The first step is the synthesis of $[Co(AA)Cl_2]$ and $[Co(BB)_2Cl_2]$ complexes, followed by the addition of the second aromatic diamine and TFSI anion. The compounds were characterized by spectral (IR and UV-VIS spectroscopy) and structural (X-ray diffraction) analysis.

Density functional theory (DFT) calculations provided optimized geometries and IR spectra. Optical absorption spectra of all complexes were simulated using the time dependent (TD) DFT method in acetonitrile solvent. The simulated spectra compare well with the experimental data, allowing for a reliable assignment of the various transitions.

We also performed DFT calculations to understand the dye regeneration mechanism of three purely organic dyes, L0, D35, and Y123, in conjunction with three different cobalt(II) complexes: $[Co(terpy)_2]^{2+}$, $[Co(bpy\text{-}pz)_2]^{2+}$, and $[Co(phen)_2(bpy)]^{2+}$, respectively. Investigation of the electron transfer from the cobalt electrolyte to the oxidized dye was performed by calculating reorganization energies for high-spin and low-spin pathways, the latter being characterized by a lower energy barrier.

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Electronic materials inspired by nature - progress in bioelectronics

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This lecture will focus on two important questions concerning biointegration of electronic devices: 1) Transduction of ionic/protonic currents into electronic ones, and 2) natural and nature-inspired semiconductors that could form the basis of such biointegratable electronics. The central idea is how both points are related – conjugated molecules found in nature could be ideal candidates for bridging biology and electronics, and indeed could change paradigms in materials science for design of organic electronic materials.

Biological systems rely on ionic and protonic currents, rather than electronic ones. Therefore a central consideration in interfacing biological matter with electronics is transduction of ionic currents into electronic ones and *vice versa*. The subject of solid state devises operating with ionic conduction will be evaluated, covering a relatively long history of research in this topic, with consideration of utility for biointegrated applications. A summary of recent demonstrations of ionic/electronic transduction in biomaterial-based devices will be presented. The second part of the talk will concern conducting and semiconducting properties of natural and nature-inspired conjugated molecules, which prominently feature the property of hydrogen-bonding interactions leading to substantial intermolecular electronic conjugation. Hydrogen bonding is responsible for supramolecular ordering in biological systems and can play a crucial role in ordering organic electrically-conducting materials as well. Recent work in applying nature-inspired H-bonded organic molecules to organic electronics devices will be discussed. Since H-bonding interactions are ubiquitous in biology, the study of H-bonded organic semiconductors is highly pertinent where interfacing of electronics and biological systems is desired.

Nanotechnology and Synchrotron Radiation for Solar Cell Materials

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Here I will talk about heterojunctions (donor/acceptor couples), molecular/substrate interfaces and novel hybrid materials for solar cells.

The combination of synchrotron radiation techniques, microscopy methods and nanotechnology design allows studying some important parameters, like the electronic structure, molecular orientation, the effect of opportune nano-structuring of the electrodes and the charge transfer time scale, that may have influence on the cells efficiency. I will show some real examples and some futuristic visions.

Laser influence on multilayer Ag/Ni and Ag/Ce magnetic thin film structures prepared by Thermionic Vacuum Arc technology

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Two multilayer Ag/Ni and Ag/Ce based thin film structures were obtained using thermionic vacuum arc method. The aim of the work was to study the morphological and structural changes, as well as changes in magnetic and electrical properties of the studied samples after laser exposure below the ablation point. A secondary purpose was to study cerium efficiency as a component for magnetic structures. Giant Magnetorezistive properties were investigated before and after the laser exposures and a comparison was made. The proposed method (TVA[1-2]) to obtain the desired structures is based on electron beam emitted by an externally heated cathode, accelerated by a high anodic voltage and a thermal evaporation method for the case of Ce - based thin films.

Two sets of samples were prepared, first a Ag/Ni multilayer structure, composed of 40 individual coatings, each with a thickness of 5 nm. The total thickness obtained for the Ag/Ni structure was 200 nm. The second interest composition, contained Ag/Ce multilayer with 39 individual coatings, with a total thickness of 140 nm. The first set of samples, namely Ag/Ni was obtained using a dual oscillating TVA discharge. For the second type of structure it was used a TVA set-up for silver, and a thermal evaporating system for cerium. A terawatt laser system was used to perform the laser exposure. The

energy of the beam was dissipated on the entire surface of 1x1 cm of the interest sample.

Structural and morphological properties were investigated using Scanning Electron Microscopy, Atomic Force Microscopy and Energy Dispersive Spectroscopy before and after laser exposure. Electrical properties of the obtained samples were studied using the 4 point measurement method, by applying a constant DC current through two of the points, and the other two were used for reading the dropping voltage on the sample. The magnetic properties were first studied before and after the laser exposure using a non-destructive optical method called MOKE (Magneto-Optical Kerr Effect). Electrical resistance behavior of the multilayer type structures was studied for different values of the magnetic field, up to 0.3 T.

[1] C. P. Lungu, I. Mustata, G. Musa, A. M. Lungu, V. Zaroschi, K. Iwasaki, R. Tanaka, Y. Matsumura, I. Iwanaga, H. Tanaka, T. Oi, K. Fujita," Formation of nanostructured Re-Cr-Ni diffusion barrier coatings on Nb superalloys by TVA method" Surf and Coat. Techn, 200 (2005) 399-402

[2] A. Marcu, C.M. Ticoş, C. Grigoriu, I. Jepu, C. Porosnicu, A.M. Lungu, C.P. Lungu, "Simultaneous carbon and tungsten thin film deposition using two thermionic vacuum arcs", Thin Solid Films, Volume 519, Issue 12 2011, P. 4074

Physical properties of different metallic oxide thin films prepared by direct thermal oxidation

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Different metallic thin films (Zn, Zn:Al, In:Sn, Ni, Ti) were deposited onto optical glass substrates by magnetron sputtering, in two configurations: perpendicular (denoted horizontal) and parallel (denoted vertical) to the plasma flow. Transparent oxide thin films (ZnO, AZO, ITO, NiO and TiO_2) were obtained by direct thermal oxidation, gradually, from room temperature (RT) to 550°C. The whole processes took place in open atmosphere. The structural, morphological, electrical and optical investigations were made for oxide thin films and, for metallic layers, respectively (when appropriate).

The structural features revealed a well-defined crystalline structure for all prepared oxide thin films and an optical transmittance higher than 60% for both, vertical and horizontal deposition arrangements. The morphological analyses were performed by atomic force microscopy (AFM), in contact mode and scanning electron microscopy (SEM). It was observed that the deposition configuration influenced the thickness and

the roughness of the prepared samples no matter of the nature of the deposited film. Electrical behavior was analyzed by van der Pauw measurements in 300 K – 50 K.

The obtained results proved that direct thermal oxidation can be an alternative in order to obtain transparent oxide thin films that can be used as buffer or dielectric layers for different electronic and optoelectronic applications.

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Magnetic nanostructures and bio-medical applications

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The remarkable new phenomena observed in magnetic nanostructures derive from the interplay between the intrinsic properties of the components, finite size effects and interphase interactions.

Two types of nanosystems with a dominant role of finite size effects and interfacial interactions will be considered in relation to their bio-medical applications: (i) multilayered magnetic systems used as bio-medical sensors and actuators and (ii) magnetic nanoparticulate systems with multiple applications (drug delivery and release, imagistics and magnetic hyperthermia). In particular, interfacial effects in layered systems and magnetic relaxation effects influencing the

magnetic response of the system with respect to a targeted bio-medical application will be discussed. Peculiar issues related to ferrofluids of different volume fractions allowing to achieve both target-specific diagnostics and therapeutics are emphasized together with proposed theoretical and experimental solving items. Specific characterization methodologies based on temperature and field dependent Mössbauer spectroscopy and SQUID magnetometry are briefly presented. The importance of the suitable magnetic characterization of nanoparticulate systems in respect to magnetic relaxation phenomena is exemplified in case of nanoparticles subjected to heating procedures (under RF fields) for cancer hyperthermia. Potential new methodologies for the correct evaluation of the specific absorption rate (SAR) from real experimental data taking into account also environmental loss factors are introduced. The whole range of heat transfer mechanisms involving large size distributions and strong inter-particle interactions are discussed as function of some relevant temperature-dependent physical parameters such as Neel and Brownian relaxation times.

Polymer solar cells on unconventional substrates - paper

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Large area production requires cost effective methods with a high production speed. Roll-to-roll printing techniques, i.e. gravure, flexography, are well established production techniques, available all over the world for printing applications and can be effectively used to produce organic solar cells. In order to employ these methods, a suitable printing support must be used.

Recently, paper was introduced as a substrate for low cost organic electronic devices. However, using paper as a substrate for organic solar cells is challenging because of the high roughness and low chemical and mechanical barrier properties which leads to absorption of the materials into the porous structure. Here we present solar cells designed to accommodate the challenges presented by the paper substrate. The air stable organic solar cells are fabricated using an inverted structure, with a metallic bottom electrode and a transparent conducting top electrode. We report 4% efficient solar cells and demonstrate that the rough surface of paper does not impede its use in high efficiency organic photovoltaics.

Van der Waals interaction in Density Functional Theory

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Most simulation studies of adsorption make the approximation that the adsorption potential can be expressed as a pairwise sum of atom-atom potentials. The pair potential is almost always taken to depend only on the separation of the two atoms. It is explicitly assumed that the adsorption potential involves only two-body interactions. Most importantly, it is often assumed that the interaction between the adatom and the substrate atoms is not influenced by the environment of the later, which clearly neglects all screening and many-body effects occurring in the substrate. The approach is questionable in, for example, the case of delocalized electrons in metallic systems.

A widely employed measure to take into account these effects is the use of effective pair potentials instead of the bare interaction potentials between the adatom and the isolated substrate atoms. In recent work, we showed that those effective potentials are no universal for the interaction between substrate materials and adatoms,

because they strongly depend on the interaction geometry: The effective potentials of an adatom with an atom embedded in a plane surface is different to the interaction with the same type of atom inside a spherical particle. Additionally, the pairwise-summation approach lacks the ability to describe anisotropy effects. These play, for example, a very important role in the binding of DNA base pairs.

The goal of our research is to describe the physical adsorption of rare-gas atoms on metal clusters without those approximations and to take into account many-body effects beyond classical screening.

The electronic ground state of the cluster is computed by means of a real-space density functional theory implementation developed in our group. We express the adsorption potential using a method that relies on the adiabatic connection dissipation-fluctuation theorem to include dispersion effects into density functional calculations. To achieve this goal, we developed a representation of the linear density-density response function that is formulated in terms of occupied Kohn-Sham orbitals only to avoid the calculation of a vast number of unoccupied states. The intermolecular repulsion at short distances is modeled by a semi-empirical potential that relies on the electronic densities. It can be universally adjusted so that *ab-initio* potentials between He and Mg, Na and Rb_2 can be reproduced.

The strength of our method is twofold. First, it belongs to the family of van der Waals density functional theory and thus it scales almost linearly with the number of electrons. This makes it applicable to large and complex systems to predict functions and properties of materials that are technologically and biologically relevant. Second, it uses the adiabatic connection dissipation-fluctuation theorem as a basic principle, which allows us to treat every interaction partner as a whole. Therefore, we are avoiding the widely used pairwise-summation approximation, which employs effective interaction potentials between the constituent atoms of the interaction partners. In our new method, this classical screening is included per construction, which makes it universally applicable to any interaction geometry. Additionally, the chemical surrounding of the substrate atoms is taken into account by ground state calculation performed by means of DFT.

Nanotechnology for Photovoltaics

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Although several photovoltaic technologies, and in general renewable energy technologies are now becoming widespread, a lot can still be done to further reduce costs, improve efficiency, and increase their much-needed contribution to the global energy portfolio. In this presentation, I will briefly review the potential of some key photovoltaic technologies, highlight the technical bottlenecks that limit full development of such potential, and describe some of the cutting-edge solutions, based on nanotechnology, that researchers worldwide are proposing - including some that are being developed in our labs.

Unconventional vortex pinning in non-centrosymmetric superconductors

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Vortex dynamics studies in non-cetrosymmetric superconductors $CePt_3Si$ and Li_2Pt_3B revealed for both compounds extremely slow movement of the flux lines in conjunction with modest critical currents. In addition, for the Li_2Pt_3B which has the highest critical current among the two superconductors (i.e. higher vortex density), the slow decay of the remanent magnetization is followed, in a certain temperature range, by avalanche-like relaxation. The apparent contradiction of extremely low relaxation rates in spite of low critical currents could be explained by the existence of an unconventional and very effective flux trapping mechanism. A possible understanding of such pinning mechanism could be the existence of fractionalized vortices. Since the superconducting phases for both $CePt_3Si$ and Li_2Pt_3B conserve time reversal symmetry the fractionalized vortices would be localized in the twin boundaries of the crystals which would then introduce strong planer barriers for flux-line motion without affecting the critical current. However, this scenario needs independent verification. This discovery might indicate a characteristic of non-centrosymmetric superconductors.

Transport in ferrocene single molecules for terahertz applications

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The transport properties of single ferrocene molecules connected to nanoscopic gold electrodes are investigated in the framework of density functional theory (DFT) calculations [1]. Our setup describes a molecular rotor, where one cyclopentadienyl (Cp) ring of the ferrocene molecule is fixed by the two electrodes, while the second ring is able to rotate. The changes in the transmission function introduced by the relative rotation angle between the two Cp rings are analyzed, which show the feasibility of the molecular device for applications in the terahertz regime.

[1] G.A. Nemnes and Adela Nicolaev, Phys. Chem. Chem. Phys. 16, 18478-18482 (2014)

Method of successive extraction of various contributions in absorption spectra of solids

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Detailed analysis of the light absorption spectra of thin films is a powerful tool in describing their band structure. In the standard method, the onset of the sharp increase of the absorption coefficient is used to determine the optical bandgap of semiconductors; this increase is due to direct allowed transitions of electrons from the top of the valence band to the bottom of the conduction band in the point Γ (centre) of the Brillouin zone. The main criterion for identifying this absorption mechanism is the relatively high value of the absorption coefficient (α) at highest measured photon energies ($h\nu$), typically α higher than 10^7 m^{-1}.

We have proposed a successive extraction procedure in determining the light absorption mechanisms for thin films. This procedure was successfully applied on In_2O_3 thin films and vanadium bronze thin films being a part of an electrochromic cell, under different applied voltages. This procedure starts with a region at the lowest photon energies, for which the absorption appears and a part of the curve can be fitted by the law $(\alpha h\nu) \sim (h\nu - E_{th})^n$, where E_{th} is the absorption threshold. The most important values of the parameter n are 1/2 (direct allowed transitions), 2 (indirect allowed transitions) and 3/2 (direct forbidden transitions). For direct transitions $E_{th} = E_g$, while for indirect transitions $E_{th} = E_g \pm E_{ph}$, where E_g is the corresponding bandgap and E_{ph} is the energy of the phonon involved in the transition. Thus obtained

values of the first contribution in the absorption coefficient are subtracted from the measured values of α. After this step, the values of the absorption coefficient in the first region have to be almost equal to zero. Other contributions are found and subtracted from the previous residuals of α, applying several times the previously explained steps.

Solar cells based on quantum structures, achievements and problems in realization

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One of the key building blocks of the future technologies is the low-dimensional crystalline structure. Silicon nanostructures are the focus of intense investigations because of their attractive electronic and optical properties. The application of nanostructured Si based materials ranges from very well assessed fields such as optoelectronic and photonics to more recent and challenging fields like future generations of solar cells. In this latter case, a continuous effort is devoted to imagine and realize cells capable to absorb the incident solar light in a wider portion of the spectrum and possibly in a more efficient way. In this respect, nanocrystals play a crucial role and understanding of their optical and electrical properties is of fundamental importance since one can in principle modulate the absorbing layer gap by simply modifying the quantum dot size. Early attempts of quantum dot solar cell have been demonstrated to be rather successful although intense research has to be still done. The ability to experimentally tailor the quantum dot size in accurate manner and study the confined modes is mandatory for many possible technological applications. Because of the small size of these systems, their distinct optical and electronic properties are considered to stem from the three-dimensional confinement of electrons and holes as well as phonons.

Although defect physics and defect related phenomena were considered to be tied with bulk properties of matter and hence irrelevant for nanostrucutres we shall see in this lecture that they are very much alive. Starting with formation of quantum dots, i.e. nucleation and precipitation we shall see that the concept of percolation, that will be introduced, needs further consideration, i.e. which model is more suitable for given conditions. This model is further linked with transport properties which are the backbone of the device and will be explored.

Titania as a photocatalyst: the effect of copper

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Titania modified with transition or coinage metals has a great potential as a photocatalyst for several reactions, in particular for the conversion of water and carbon dioxide into hydrocarbons. More specifically, we are interested in copper, which has been shown to improve the activity of titania for these reactions.

However, the role of copper in the overall mechanism has still to be clarified in relation to the elementary processes taking place in the photocatalyst, in the photoabsorption, in the charge separation and in the chemical reactions taking place on the system. To shed light on these aspects, first-principles simulations based on density functional theory have been performed in two cases: copper doping in bulk titania and copper particles on titania surfaces. Copper doping induces important changes in the local atomic structure of both polymorphs rutile and anatase, mainly due to its different oxidation state with respect to titanium.

Adatoms and particles on the (101) and (100) surfaces of anatase were investigated as well. In this case, the presence of copper can lead to changes in the edges of valence and conduction bands, but also to the appearance of mid-gap states, depending on the atomic structure of the cluster and the coordination of the copper atoms. Regardless whether copper is present in the bulk or at the surface of titania, its presence has an effect on the local atomic structure of the semiconductor, as well as on the electronic structure of the system. This should have consequences both for the photoabsorption process and for subsequent dynamics of the photogenerated excitations.

Breakdown and wear-out phenomena in high-*k* dielectrics

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In the last decade a considerable progress has been made in understanding the electrical and material properties of high-*k* dielectrics. As a result, one of the main criteria for their implementation in advanced CMOS technologies – low enough leakage current for equivalent oxide thickness below 1 nm – has been successfully fulfilled. The next important challenge in integrating these materials is to achieve lifetimes equal or better than those of the SiO_2 counterparts. However, due to a lack of generally accepted breakdown (BD) model for high-*k* dielectrics, it is difficult to evaluate their real lifetime. To overcome this situation, a deeper understanding of physical mechanisms of wear-out and breakdown phenomena in these materials, which might be substantially different from those in SiO_2, is needed.

One of the peculiarities of high-*k* thin films is their "trap-rich" nature. Even in virgin devices (not electrically stressed) a considerable amount of pre-existing traps are present. They play an important role in dielectric wear-out and presumably affect the BD process. The second one is their double-layer structure i.e. the presence of SiO_2-like interfacial layer between the high-*k* bulk and Si-substrate. This introduces asymmetry in the band structure and leads to polarity dependence of the leakage and reliability properties. A number of experimental data are available which indicate that the reliability of high-*k* dielectrics, at least under gate injection, is controlled by the breakdown of the interfacial layer rather than the high-*k* layer itself. The attempts to clarify whether the breakdown is dominated by intrinsic or extrinsic mechanisms by analyzing the area and thickness dependence of breakdown distributions, so far have given only a limited insight into this issue. While area scaling is mostly consistent with Weibull statistics, demonstrating that intrinsic effects rather than manufacturing induced defects (extrinsic ones) control the breakdown, the experimental evidences regarding thickness dependence are still contradictory. Depending on the specific high-*k* material (Al_2O_3, ZrO_2, HfO_2), as well as on the technological history of the samples, the breakdown distributions exhibit different thickness dependence – some of them support the concept of intrinsic mechanisms and others are consistent with extrinsic ones. Thus, the present status, does not allow making general conclusions about degradation mechanisms in high-*k* materials.

The focus in this presentation will be put on the reliability properties of Ta_2O_5 – based dielectrics. Time-dependent-dielectric-breakdown (TDDB) characteristics measured under constant-voltage-stress (CVS) and their dependence on stress voltage and temperature for Hf-doped Ta_2O_5 will be presented and discussed. They are compared with similar experimental data for undoped Ta_2O_5 in order to investigate the effect of doping. The comparison shows improved TDDB characteristics in doped

films with regard to the pure ones. The presence of Hf into the matrix of Ta_2O_5 modifies the breakdown mechanism making it more adequate to the percolation model. Some results concerning the effect of the metal gate on the breakdown properties and the wear-out of the interfacial layer during electrical stress will be also presented.

The asymmetric well: a way to understanding core-shell quantum dots

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The core-shell quantum dots are subject of intense investigation, due to the tunability of their band gap. The radial equation of an electron moving in such a quantum dot with zero angular momentum is identical with that of a particle moving in an one-dimensional, asymmetric rectangular square well. Using the approximate analytical expressions of the energy of bound states in a symmetrical well, the energy of the bound states in a slightly asymmetric well are obtained.

They are given by approximate analytical formulas, with error of about 10^3; for reasonable parameters of the well. These results are obtained using algebraic approximations for the trigonometric functions entering in the transcendental equation for the energy eigenvalues.

[1] Cotton, S. *Lanthanide and actinide chemistry*, John Wiley & Sons, New York, **2006**.
[2] Costes, J. –P.; Dahan, F.; Wernsdorfer, W. *Inorg. Chem.* **2006**, *45*, 5-7; (b) Ishikawa, N.; Sugita, M.; Wernsdorfer, W. *J. Am. Chem. Soc.* **2005**, *127*, 3650-3651.
[3] Paulovic, J.; Cimpoesu, F.; Ferbinteanu, M.; Hirao, K. *J. Am. Chem. Soc.* **2004**, *126*, 3321-3331; (b) Ferbinteanu, M.; Kajiwara, T.; Choi, K. –Y.; Nojiri, H.; Nakamoto, A.; Kojima, N.; Cimpoesu, F.; Fujimura, Y.; Takaishi, S.; Yamashita, M. *J. Am. Chem. Soc.* **2006**, *128*, 9008-90009.
[4] Tanase, S.; Ferbinteanu, M.; Cimpoesu, F., *Inorg. Chem.* 2011, 50(19), 9678-9687. (b) Ferbinteanu, M.; Cimpoesu, F.; Gîrtu, M. A.; Enachescu, C.; Tanase, S. *Inorg. Chem*. **2012**, 51, 40-50. (c) Cimpoesu, F.; Dahan, S.; Ladeira, S.; Ferbinteanu, M.; Costes, J.-P. *Inorg. Chem*. **2012**, 51, 11279-11293.
[5] Ramanantoanina, H.; Urland, W.; Cimpoesu, F., Daul, C. *Phys. Chem. Chem. Phys.*, **2013**, *15*, 13902; (b) H. Ramanantoanina, H.; Urland, W.; García-Fuente, A.; Cimpoesu, F.; Daul, C. Daul, *Chem. Phys. Lett.*, **2013**, *588*, 260. (c) Ramanantoanina, H.; Urland, W.; Cimpoesu, F., Daul, C. *Phys. Chem. Chem. Phys.* **2014**, *16*, 12282-12290.

Nano Approach to more Effective Electrode Materials for Lithium and Sodium Ion Batteries

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The functional properties of many oxide-based materials are critically dependent on their atomic arrangement on a nanometric scale. Therefore, linking the macroscopic properties with the local structure of constituent atoms is an important research topic in modern materials chemistry and open new opportunities for engineering the materials with preset properties.

Cathode materials for lithium ion batteries comprise several groups of compounds, the most interesting being lithium transition metal oxides with layered structure. The electrochemical reaction includes a reversible lithium intercalation into host electrode materials concomitant with reversible redox reaction of transition metal ions. The good lithium reversibility of the oxides is a consequence of their ability to uptake various Li-ion concentrations without suffering irreversible structural changes.

Rechargeable sodium ion batteries operate in the same way like as lithium-ion batteries: by a reversible sodium intercalation between electrodes. Because sodium is heavier and has lower redox potential than lithium, sodium ion batteries exhibit lower energy density. However, the big environmental concerns give nowadays the impetus for development of sodium ion batteries. To become sodium ion technology feasible, novel electrode materials are needed.

This contribution aims to outline the relations between the nanoscale effects and electrochemical properties of lithium and sodium transition metal oxides with layered crystal structure and compositions of $LiCo_{1-2x}Ni_xMn_xO_2$ ($0.01 \leq x \leq 0.5$) and $Na_yCo_{1-2x}Ni_xMn_xO_2$ ($0.5 \leq y < 1, x = 1/3, 1/2$). The local structure is determined by applying two complementary spectroscopic techniques: high-frequency electron paramagnetic resonance spectroscopy and solid state nuclear magnetic resonance with ultrafast magic angle spinning rates. The electrochemical properties of the oxides are examined in model lithium cells. The capability of layered oxides to exchange lithium and sodium ions are presented and discussed in terms of development of sodium ion batteries as a green alternative to the lithium ion batteries. The synthesis and structural characterization of substituted sodium-manganese oxides are also provided. The specific structure of substituted sodium-manganese oxides enables a rapid exchange of Na^+ with Li^+, which on its turn determines their potential for direct use as cathode materials in lithium ion batteries.

Electrons in 2D isospectral shapes: phase extraction and few-particles properties

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The remarkable discovery of non-congruent, yet isospectral 2D shapes by C. Gordon *et al.* [1], followed more than a quarter century after the debate was launched by M. Kac [2], and immediately captured significant attention, not only from mathematicians, but from physicists as well. All systems obeying Helmholtz's equation $(\nabla^2 + \mathrm{E}) = \Psi$ are candidates for experimental testing of isospectrality, as was the case of electromagnetic waves in cavities [3] or electrons in nanostructures [4]. The latter set-up was proven to allow also the extraction of the eigenmodes phases (i.e. the position of nodal lines), based on a special property, called transplantation, which relates the eigenfunctions of the isospectral pairs, thus bringing supplementary information and allowing to extract the phase distributions, if the amplitudes distributions are known.

In this context, we theoretically study the effect of inherent experimental imperfection -disorder, edge roughness, or interaction effects- on the phase extraction in isospectral shapes and our numerical results indicate a certain robustness, meaning that a reliable phase extraction can be performed if the misfit of the wave function is below 5% [5].

Few-particles properties of the two isospectral shapes (called Bilby and Hawk) are also discussed, applying the configuration-interaction method in a finite-differences model.

[1] C. Gordon, D. Webb, S. Wolpert, Inventiones Math. **110**, 1 (1992).
[2] M. Kac, Am. Math. Mon. **73**, 1 (1966).
[3] S. Sridhar, A. Kudrolli, Phys.Rev.Lett. **72**, 2175 (1994).
[4] C.R. Moon, L.S. Mattos, B.K. Foster, G. Zeltzer, W. Ko, H.C. Manoharan, Science **319**, 782 (2008).
[5] M. Ţolea, B. Ostahie, M. Niţă, F. Ţolea, A. Aldea, Phys.Rev.E**85**, 036604 (2012).

Single crystal superconducting oxides: from precursors to devices. Is a novel X-ray lithography possible?

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Superconducting oxides with critical temperatures T_c of the order of 90 K are presently widely investigated both from the point of view of basic research (e.g. electron pairing mechanism, THz emission, etc.) and of their applications (e.g. power cables, electromagnetic coils, asynchronous motors, etc.). Among them, the non-stoichiometric oxides $Bi_2Sr_2CaCu_2O_{8+x}$ (Bi-2212) and $YBa_2Cu_3O_{7-\delta}$ (Y-123) are probably the most extensively studied compounds, with maximum T_c of about 85 and 92 K, respectively. In both materials the non-stoichiometric O content represents a key feature, deeply affecting both their electronic properties and their crystal structure. Therefore, the combined use of X-ray diffraction (XRD) and of electrical/magnetic measurements provides crucial information on the O content of these systems and its realationship with their superconducting properties.

Here we present an overview of some results concerning the growth of single crystals with high aspect ratio (whiskers) and the effects of different post-growth treatments affecting the properties of final devices.

About Y-123, we have shown that it is possible to induce a simultaneous Ca and Al co-doping of the system, where Al ions are incorporated in the structure only at a specific Cu site, while Ca can substitute both Y and Ba sites. Although the final amount of the doping species in the crystals is not fully predictable, a transition from the orthorhombic to the tetragonal system takes place with increasing the Al content, while the superconductivity of the system is reduced and finally disappears. Concerning Bi-2212, we have also proved that the temperature of the synthesis process affects both the *c*-axis lattice parameter and the T_c of the crystals, testifying that the O content is decreased when the temperature is increased. In spite of the fact that the thermodynamics of Bi-2212 and Y-123 is quite different, several evidences from high resolution transmission electron microscopy (HRTEM) and XRD indicate that whiskers of both materials actually share a common growth mechanism. Indeed, mapping different regions of curved crystals by means of a synchrotron radiation nanoprobe has proved that the axis orientation is fixed regardless of the crystal habit, setting the size changing, moving and multiple growth interface (SCMMGI) mechanism as the most likely process for their common origin.

Moreover, we have also investigated the possibility of tuning the O content of these crystals after their growth. It has turned out that an annealing process in air at 90°C can effectively reduce the O amount of Bi-2212 crystals, as shown by both XRD data and their transport properties. However, the most striking observation is that the O amount can also be modified *locally* by means of a synchrotron radiation nanoprobe via

some mechanism that seems to be non-thermal in nature. Indeed we have irradiated Bi-2212 single crystals by means of a 17 keV beam with space resolution of 117 □ 116 nm^2 up to a maximum dose of about 3×10^{12} Gy, observing a monotonic behavior with a maximum increase in the critical temperature T_c of 1.3 K and a maximum elongation of about 1 Å in the *c*-axis length, compared to the as-grown crystals [1]. These facts clearly testify a change in the Bi-2212 doping level, which shows close similarity to the appearance of a two-dimensional electron gas in $SrTiO_3$ after exposure to UV synchrotron light [2].

These results support the possible use in the future of hard X-rays as a novel direct-writing, photoresist-free lithographic method for these compounds with potential nanometric spatial resolution.

[1] Alessandro Pagliero *et al*., Nano Lett., 14, 1583 −1589 (2014)
[2] W. Meevasana *et al*., Nature Mater., 10, 114-118 (2011)

Adsorption and photoactivation of probe molecules on transition metal oxide nanoclusters and molecular complexes. Reaction mechanism of conversion to fuel

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Transition metal oxide clusters possess photo-reactivity, which cannot be predicted straightforward. The adsorption and activation of carbon dioxide by cuprous oxide (Cu_2O) clusters, nanoclusters and nanolayers have been examined by density functional theory, using the B3LYP and HSE06 density functionals. The structures of $Cu_{32}O_{16}$ and $Cu_{14}O_7$ clusters have similar features and bear elements from the bulk Cu_2O – linear OCuO units and tetrahedral oxygen anions. The clusters and nanolayers form copper dimers and larger copper ensembles on their surface. For the reduction of carbon dioxide, water dissociation has been considered as a source of hydrogen. In the presence of coordinatively unsaturated oxygen atoms on the surface of Cu_2O thin layers and clusters, water dissociation is spontaneous. Carbon dioxide adsorbs either end-on, on terminal copper centers, or by formation of surface carbonate species. The first step of CO_2 hydrogenation is also spontaneous as the calculated energy barrier is only 7 kJ mol^{-1}. It results in the formation of hydroxylated intermediate, –CO(OH). The second step of reduction with formation of CH-bond is energetically more demanding as the calculated barrier is 121 kJ mol^{-1}. The surface copper ensembles play important role in adsorption and reaction, because copper atoms easily pop-up to participate in bond formation with adsorbate molecules.

Nano-Confined Polymer Structures for Adhesive Protein Binding

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Summary

We present a stimulated emission depletion (STED) lithography approach for the fabrication of sub-100 nm polymeric structures [1-3]. Protein-adhesive polymers allow for biofunctionalization down to a single protein level [3].

Introduction

STED lithography is a powerful tool for maskless 3D structuring far below the resolution limit with any desired geometry [1-5]. First, a pulsed NIR-laser creates a spatially confined volume of excited photo-initiators by multi-photon-absorption. The focus of a second laserbeam is shaped like a donut to yield an intensity distribution with a central hole in order to deactivate the photoinitiators in the outer rim via stimulated emission. This yields a restriction of the excitation volume. Similar to STED-microscopy [6,7], the excitation volume and thus the polymerization volume is reduced.

The ability to place individual proteins onto nano-confined structures plays a constantly growing role in bioscience. Spatial patterning of surface properties (e.g. chemical or physical), has been used to control and investigate the behavior of cells [8-10]. Using STED lithography, we are able to produce nano-confined features that can be used to immobilize and present single proteins on defined places [3].

Results

Using a 110 fs pulsed laser (780 nm) for two-photon polymerization (TPP) and a 532 nm CW laser for STED, we are able to obtain structure sizes of 55 nm in all three dimensions (Fig. 1) and manufacture two clearly separated lines with 120 nm lateral distance, which marks the best resolution in STED lithography reported so far [1,2].

Acrylate nanostructures with various sizes are fabricated on a poly(ethylene) glycol (PEG) functionalized glass surface via STED lithography. For nanoscopic characterization of the protein density and localization of individual proteins we use direct stochastic optical reconstruction microscopy (dSTORM) (Figure 2) [11].

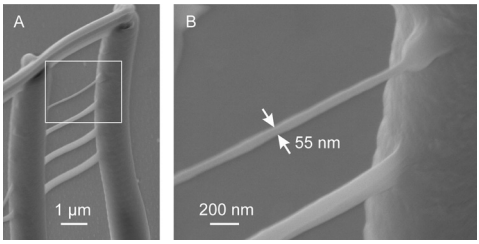

Fig 1. A) Electron micrograph of a polymerized structure: two poles with a horizontal bar on top act as a frame, fabricated with two photon polymerization. The rungs are written with the additional STED-beam with different intensities. B) shows a zoom of a rung with a thickness of 55 nm [2].

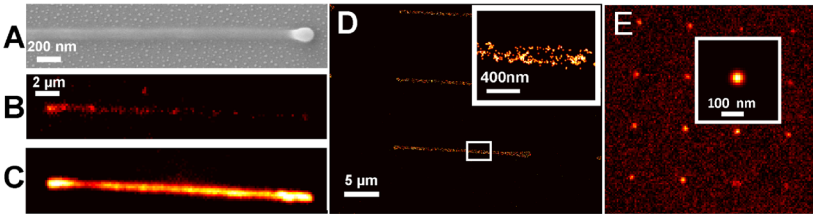

Fig 2. A) Electron micrograph of TPP written lines. B) Fluorescent image of the same polymer line (low autofluorescence prior to metallization). C) Polymer line after functionalization with fluorescent antibodies. D) dSTORM image of TPP lines after functionalization. E) Fluorescence image of functionalized nanoanchors, inset shows detail of dSTORM image [3].

Conclusion

Using STED lithography allows fabrication of nanoscopic polymer structures with defined chemical properties. Using 780 nm for TPP and 532 nm for STED, single features with 55 nm in size are fabricated (λ/14 for 780 nm excitation) and a lateral resolution of 120 nm is achieved. Combining STED lithography and dSTORM imaging allows us to produce well characterized, biocompatible structures, applicable to many biological assays.

References

[1] R. Wollhofen et al., *Optics Express*, **21**, 10831, 2013
[2] T. A. Klar et al., *Physica Scripta*, in print
[3] M. Wiesbauer, R. Wollhofen et al., *Nano Letters*, **13**, 5672, 2013
[4] J. Fischer et al., *Advanced Materials*, **22**, 3578, 2010
[5] J. Fischer et al., *Laser & Photonics Reviews*, **7**, 22, 2013
[6] T. A. Klar and S. W. Hell, *Opt Lett*, **24**, 954, 1999
[7] T. A. Klar et al., *Proc Natl Acad Sci*, **97**, 8206, 2000
[8] J. Hesse et al., *Genome Res*, **16**, 1041, 2006
[9] R. Schmidt et al., *Journal of Proteome Research*, **10**, 1316, 2011
[10] B. L. Aekbote et al., *European Polymer Journal*, **48**, 1745, 2012
[11] S. van de Linde et al., *Journal of Structural Biology*, **164**, 250, 2008

Large area surface nanopatterning by ultrafast laser pulses

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The ultrashort pulsed lasers are intensively used for fundamental research and technological developments in the field in material processing and characterization. Due to the short pulse duration, shorter than the thermal diffusion time of most of the materials, the heat affected zone of the irradiated area remains confined below the size of the focused laser spot. Then, femtosecond and picosecond laser pulses can precisely process the materials at sub-micrometer level. However, when large area has to be processed, the total processing time becomes a technological issue.

In this work two approaches for fast laser processing of large area are presented. The first one is based of self organization of quasi-periodical surface nanostructures induced by laser irradiation in ultrafast laser pulses regime. The Laser Induces Periodical Surface Structures (LIPSS) appears almost on all type of materials. Their orientation can be controlled by the polarization of the laser. The morphology depends on the substrate type, as well as on the laser beam parameters such as laser intensity, number of pulses, pulse duration and temporal pulse shape.

The second method for large area processing is based on optical near-field enhancement of single femtosecond laser pulses using transparent mask as optical concentrators. Transparent mask are produced in photoresists and used as focusing micro-optics for laser ablation of structures below the diffraction limit. Potential applications of laser nano-textured surfaces are also discussed.

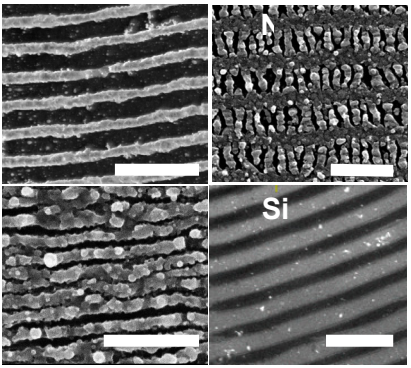

Fig. 1. LIPSS on various materials. Scale bar is 1 μm.

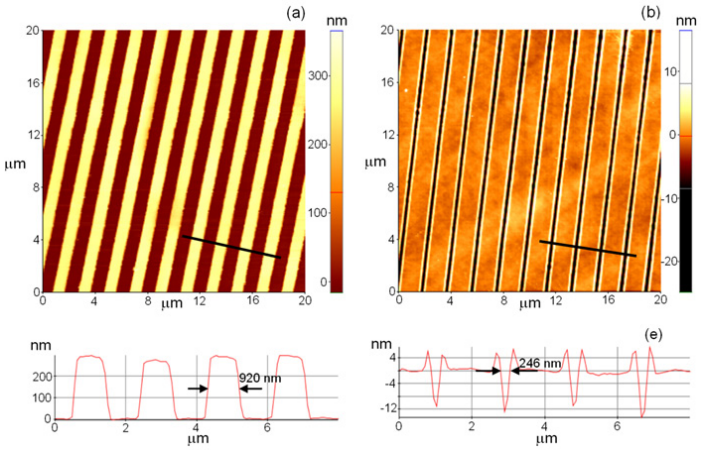

Fig. 2. The AFM image of the photoresist mask (a);
The imprinted pattern produced by near-field laser ablation.

References

[1] C. Albu et al., Periodical structures induced by femtosecond laser on metals in air and liquid environments, Appl. Surf. Science 278, 347-351 (2013).
[2] M. Zamfirescu et al., The role of the substrate material type in formation of laser induced periodical surface structures on ZnO thin films, Appl. Surf. Science 258, 9385-9388 (2011).
[3] Florin Jipa et al., Laser parallel nanofabrication by single femtosecond pulse near-field ablation using photoresist masks, Optics Express 22, 3356-3361 (2014).