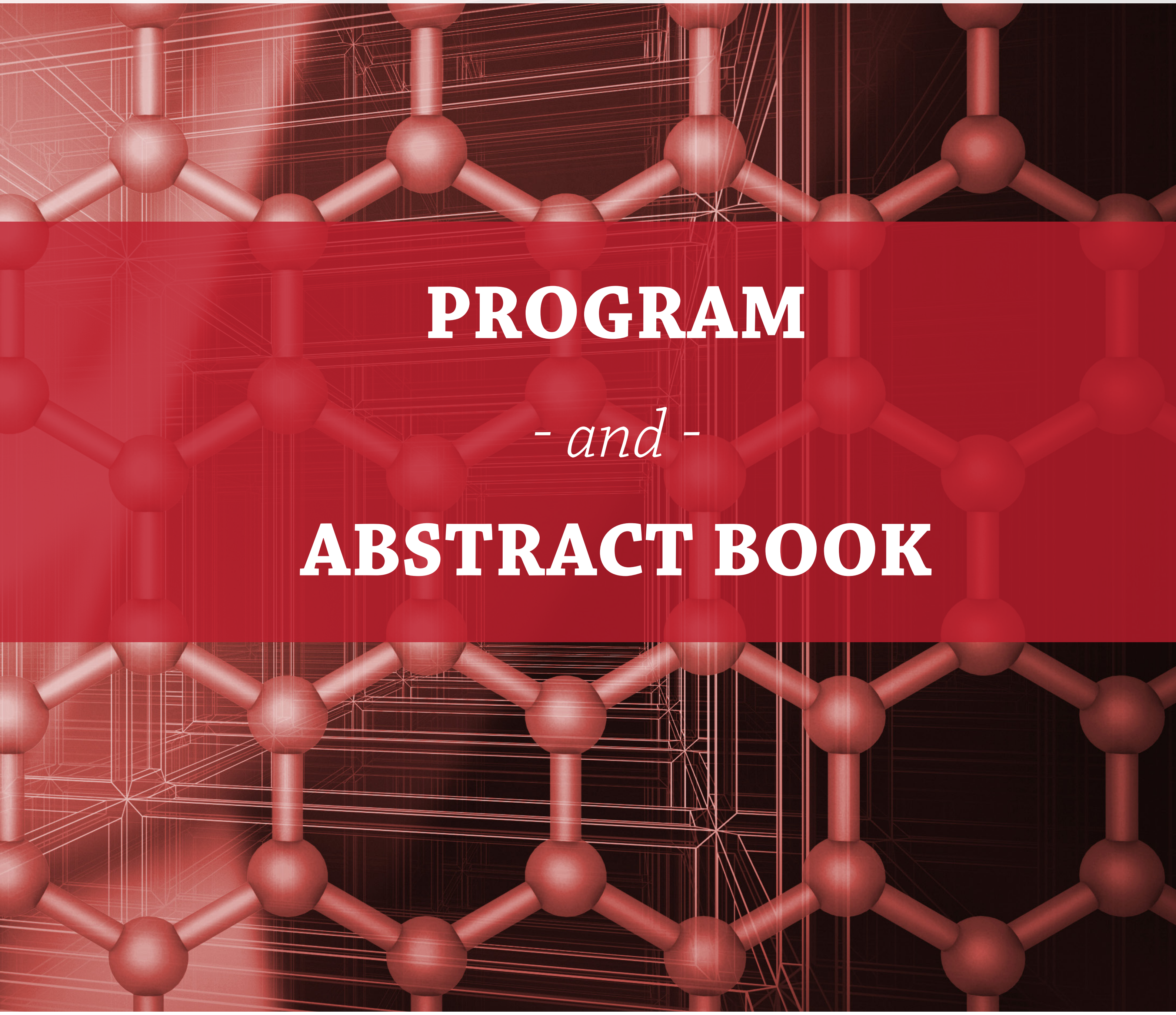
INTERNATIONAL WORKSHOP OF MATERIALS PHYSICS



PROGRAM

- and -

ABSTRACT BOOK

ORGANIZED BY :

Fundația "Cultură și Fizică la Măgurele"

INTERNATIONAL WORKSHOP OF MATERIALS PHYSICS

The National Institute of Materials Physics (NIMP) is a lead scientific institution in Romania, determined to become an excellence research center at European level. Its current research topics are related to solid state physics and materials science, with special focus on oxide materials, organic-inorganic composites and hybrid structures, dedicated for applications ranging from electronics and life sciences to green energy or nuclear fusion reactors. The Institute has a modern infrastructure, covering various preparation/deposition methods and a wide number of characterization techniques, highly qualified personnel and a significant number of collaborations with research institution from abroad.

The International Workshop of Materials Physics organized by NIMP aims at becoming a periodic forum in the exchange of ideas between the local researchers and distinguished members of the international research community in the field. Presentations will be both related to scientific breakthroughs and success stories of applications of research results in industry.

Accordingly, the extra - scientific topics of the workshop for its first edition will be covering the following aspects:

- *Connecting NIMP to new hot research topics* with the aim to develop new collaborations of high potential success for EU project applications (with special emphasis on novel materials and interface with life sciences)
- *Increasing attractiveness for foreign researchers* to come and work at NIMP (with the possibility to apply for ERA-Chair projects or ERC grants)
- *Increasing the performance and improving the image of NIMP's researchers* in order to successfully apply for ERC grants (learning from the experience of ERC grantees)
- *Learning good practices for improving excellence in research*, with special emphasis on the innovative aspects and the general relation with the industry (including discussions regarding application for TEAMING and TWINNING projects)

CHAIR

Lucian PINTILIE
National Institute of Materials Physics, Bucharest, Romania
E-mail : pintilie@infim.ro

LOCAL ORGANIZERS

Jean Narcis BARASCU
National Institute of Materials Physics, Bucharest, Romania
Mona CHIRITOI
National Institute of Materials Physics, Bucharest, Romania
Cristina MILITARU
National Institute of Materials Physics, Bucharest, Romania
Teodora PINTILIE
National Institute of Materials Physics, Bucharest, Romania

PROGRAM

23RD OF MAY 2016

08:30 - 09:00	***Registration***
09:00 - 09:15	***Opening (General Director of NIMP)***

CHAIR : Ionut ENCULESCU — *ELECTRONICS*

09:15 - 09:45	**Rodrigo MARTINS** *“Exploiting Paper as Active Component in Novel Transistor Architectures”*
09:45 - 10:15	**Elvira FORTUNATO** *“Why metal oxide nanoparticles are so interesting?”*
10:15 - 10:30	**Radu DRAGOMIR** *“Selective exchange effects in single-Mn doped quantum dots”*
10:30 - 10:45	**Camelia FLORICA** *”High performance field effect transistors based on single ZnO nanowires”*
10:45 - 11:00	***COFFEE BREAK***

CHAIR : Cristian Mihail TEODORESCU — *ULTRA-THIN and 2D*

11:00 - 11:30	**Nick BARRETT** *“Electron spectromicroscopy of ferroelectric oxides”*
11:30 - 12:00	**Marin ALEXE** *“Topological structures and torroidal ferroelectricity in ultra-thin films and devices”*
12:00 - 12:30	**Silvano LIZZIT** *“Synchrotron radiation photoemission and photoelectron diffraction: the 2D materials case”*
12:30 - 12:55	**Angelo AGOSTINO** *“Synchrotron light for material characterization and modification in the frameworks of international projects”*
12:55 - 13:10	**Laura ABRAMIUC** *“Photoelectron spectromicroscopy of $Pb(Zr,Ti)O_3$(001) and (111) surfaces”*
13:10 - 14:30	***LUNCH***

CHAIR : Ioana PINTILIE — *ENERGY*

14:30 - 15:00	**Thomas RATH** *“Research on Emerging Materials for Hybrid Photovoltaics at Graz University of Technology”*
15:00 - 15:30	**Alexandru NEMNES** *“Ab initio calculations of the band alignment in halide perovskite solar cells”*
15:30 - 16:00	**Daniel VIZMAN** *“New trends in directional solidification of multicrystalline silicon for photovoltaic applications”*
16:00 - 16:15	**Cristina BESLEAGA-STAN** *“Stability in perovskite solar cells“*
16:15 - 16:30	**Neculai PLUGARU** *“Atomistic simulations of methylammonium lead halide layers on $PbTiO_3$ (001) surfaces“*

16:30 - 16:45	***COFFEE BREAK***
16:45 - 18:00	**ROUND TABLE** *EU priorities in materials research (co-chairs Rodrigo Martins, Elvira Fortunato)*
19:00 - 22:00	***DINNER***

24TH OF MAY 2016

CHAIR : Aurelian-Catalin GALCA — *FUNCTIONALITIES*

09:00 - 09:30	**Guus RIJNDERS** *“Long range symmetry propagation initiated at heterostructure interfaces”*
09:30 - 10:00	**Viorel POP** *“Hard Magnetic Materials with Reduced Rare-Earth Content”*
10:00 - 10:15	**Andra-Georgia BONI** *“Influence of interlayer type on ferroelectric/dielectric characteristics of multilayered structures”*
10:15 - 10:30	**Ion IVAN** *“AC driven magnetic flux quanta in YBCO composite thin films with complex pinning structures”*
10:30 - 11:00	***COFFEE BREAK***

CHAIR : Mariana STEFAN — *LARGE INFRASTRUCTURES*

11:00 - 11:30	**Jana KOLAR** *“CERIC-ERIC - European Research Infrastructure Consortia and Materials Science in Central East Europe”*
11:30 - 12:00	**Primož ŠKET** *“SLONMR: From small organic compounds to macromolecules”*
12:00 - 12:30	**Marek STANKIEWICZ** *“SOLARIS - new synchrotron light source in Europe”*
12:30 - 12:45	**Nicoleta APOSTOL** *“Chemistry of carbon and carbon monoxide on Pb(Zr,Ti)O_3(001) surfaces”*
12:45 - 13:00	**Raluca NEGREA** *“Electron microscopy at NIMP: capabilities and collaboration opportunities”*
13:00 - 13:20	*Presentation from Carl-Zeiss*
13:20 - 14:45	***LUNCH***

CHAIR : Victor KUNCSER — *MATERIALS FOR LIFE SCIENCES, CATALYSIS*

14:45 - 15:15	**Mangala SRINIVAS** *"Nanoparticles for multimodal clinical and preclinical in vivo imaging"*
15:15 - 15:45	**Nicoleta LUPU** *”Low T_C Glassy Magnetic Alloys for Medical Applications”*
15:45 - 16:15	**Vladimír MATOLÍN** *“Thin film catalysts for fuel cell technology”*

16:15 - 16:30	**George STAN** *“Dental implant fixtures bio-functionalized with mechanically resistant and cytocompatible bioglass coatings by magnetron sputtering technique”*
16:30 - 16:45	**Ovidiu CRISAN** *“Nanoparticles and nanoclusters versatile synthesis methods: pathway towards integrated devices for nanosensing and biomedical applications”*
16:45 - 17:00	***COFFEE BREAK***
17:00 - 17:45	*How to write a successful application (ERC, Horizon 2020)?*
19:00 - 22:00	*Dinner sponsored by Carl-Zeiss*

25TH OF MAY 2016

CHAIR : Mihaela BAIBARAC — *CARBON AND NANO*

09:00 - 09:30	**Mircea DRAGOMAN** *“Beyond graphene: hundreds of atomically thin materials”*
09:30 - 10:00	**Magdalena TITIRICI** *“Sustainable Carbon Materials and Chemicals from Biomass Hydrothermal Processes”*
10:00 - 10:15	**Adelina MATEA** *“Anti-Stokes Raman spectroscopy as a method to identify metallic and mixed metallic/semiconducting configurations of multi-walled carbon nanotubes”*
10:15 - 10:30	**Ana Maria LEPADATU** *“Morphology-driven charge storage properties of trilayer structures with Ge nanocrystals in HfO$_2$”*
10:30 - 11:00	**Russell BINIONS** *“Functional metal oxide thin films from electric field assisted aerosol assisted chemical vapour deposition”*
11:00 - 11:30	***COFFEE BREAK***

CHAIR : Lucian PINTILIE — *FUNCTIONALITIES*

11:30 - 12:00	**Steve DUNN** *“Photoinduced carrier dynamics – the ferroelectric dipole’s influence on recombination”*
12:00 - 12:30	**Mihai GIRTU** *“Research in Materials Physics at Ovidius University of Constanta”*
12:30 - 12:55	**Augusto Claudio MARCELLI** *“Nanoscale phase separations in quantum materials”*
12:55 - 13:10	**Iosif-Daniel SIMANDAN** *“Photoexpansion in a-As$_2$S$_3$: a possible new mechanism”*
13:10 - 13:25	**Cristian SIMION** *“Transducing mechanism of ammonia detection using BaSrTiO$_3$”*
13:25 - 13:30	***CLOSING***
13:30 - 15:00	***LUNCH***

ELECTRONICS

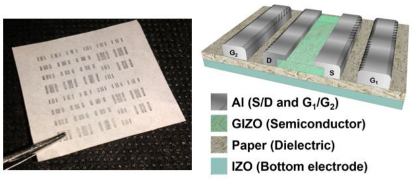
Exploiting paper as active component in novel transistor architectures

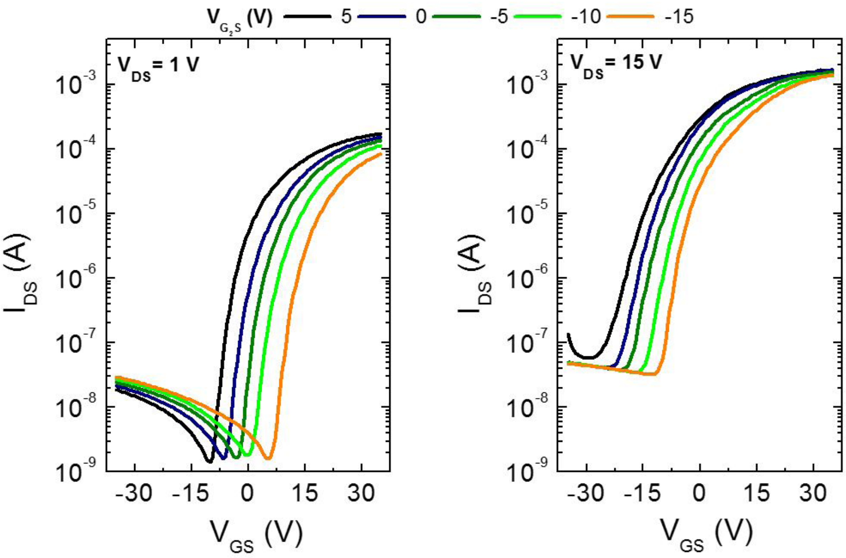
R. MARTINS, L. Pereira, D. Gaspar, E. Fortunato

ii3N/CENIMAT, Department of Materials Science, Faculty of Science and Technology,
Universidade NOVA de Lisboa and CEMOP/UNINOVA, Campus de Caparica, 2829-516 Caparica, Portugal

E-mail: rm@uninova.pt

In this presentation we aim to present the set of developments achieved at CEMOP/CENIMAT concerning the exploitation of paper, besides substrate as a truly electronic component, emphasizing its role in developing new thin film transistor architectures for spongy-based dielectric devices, where a high leakage and high recombination rate of free carriers at dielectric to semiconductor interface are foreseen. In these architecture two in-plane gates with drain and source are produced, while in the opposite side it is located a floating gate, constituted by high conductive oxide, whose function is to storage/control free carriers. This induces a potential between the floating electrode and the paper dielectric that prevents free carriers to be lost. In the structure discussed the channel is based in gallium indium zinc oxide 40-60 nm thick, while the dielectric is cellulose paper, with a thickness of about 70 µm. The simulated transfer characteristics of these devices under low and high drain to source voltages will be discussed (see figure above) and compared with the set of experimental results achieved. Overall we notice that the device performances are equal or superior to the ones of devices using paper as dielectric in a staggered bottom gate configuration, with an ION/IOFF ratio above 104 and a saturation mobility of ≈ 3 $cm^2V^{-1}s^{-1}$. The dual gate planar configuration allows controlling the on-voltage of the transistors in a broad range, moving the on voltage from depletion to enhancement region, function of the drop potential established between both gates. The advantages of having devices full developed in plane will be discussed, when compared with the traditional known configurations.





Key Words: *Paper Electronics; Thin Film Transistors; Novel Device Architectures*

Acknowledgements: *This work was funded by European Projects A3Ple (FP7, NMP-2010-SME-4 grant 262782), NewFun (ERC-StG-2014, grant GA 640598) and BET-EU (H2020-TWINN-2015, GA 692373). Thanks are also due to project EXCL/CTM-NAN/0201/2012, the FEDER funds through the COMPETE 2020 Programme under the project UID/CTM/50025/2013.*

Why metal oxide nanoparticles are so interesting?

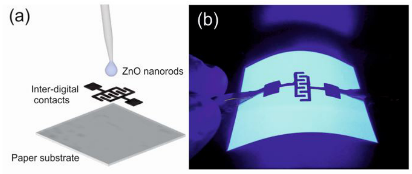
E. FORTUNATO, L. Santos, A. Gonçalves, A. Pimentel, D. Nunes, A. Marques, R. Martins

*i3N/CENIMAT, Department of Materials Science, Faculty of Science and Technology,
Universidade NOVA de Lisboa, Campus de Caparica, 2829-516 Caparica, Portugal*

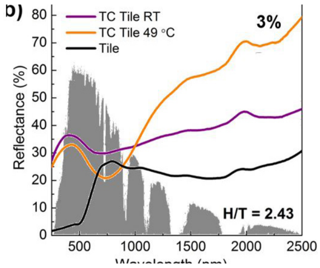
E-mail: emf@fct.unl.pt

In this paper we refer the work performed within i3N/CENIMAT in the area of functional metal oxide nanoparticles to be used in a wide range of applications, as it will be exemplified in the following text.

ZnO NPs - ZnO nanostructures have been produced either under microwave irradiation using low cost domestic microwave equipment or by conventional heating, both under hydrothermal conditions. X-ray diffraction, scanning electron microscopy, Fourier transform infrared spectroscopy, room/low temperature photoluminescence and Raman spectroscopy have been used to investigated the structure, morphology and optical properties of the produced ZnO nanorods. The hexagonal wurtzite structure has been identified, and a red-orange emission has been detected in the presence of UV irradiation for all the conditions studied. The as-prepared ZnO nanorods were test as a UV sensor on paper substrate, which lead to a fast response and a rapid recovery times, as well a sensitivity up to 10 indicating that these materials may have a high potential to be employed in low cost, disposable UV applications.



VO2 NPs - The capability to control in an smart way the infrared reflectance to environmental temperature variations, can be achieved with thermochromic materials like VO2. In this paper we report by the first time a new application of VO2 on ceramic tiles, aiming to control the reflected IR radiation on smart roofs and thus improving the energy efficiency as possible and reducing the carbon dioxide emissions. The VO2 NPs have been produced by hydrothermal synthesis, providing a new, quicker and cleanner production route. The superior thermochromic characteristics of VO2 nanoparticles in conjunction with this new application to a smart roof offers a great potential to regulate the energy in an intelligent way.



WO3 NPs - Electrochemically active bacteria have the capability to transfer electrons to cell exterior, a feature that is currently explored for important applications in bioremediation and biotechnology fields. However, the number of isolated and characterized EAB species is still very limited regarding their abundance in nature. Colorimetric detection has emerged recently as an attractive mean for fast identification and characterization of analytes based on the use of electrochromic materials. In this work, WO3 nanoparticles were synthesized by microwave assisted hydrothermal synthesis and used to functionalize non-treated regular copy-paper substrates. This allowed the production of a paper-based colorimetric sensor able to detect EABs in a simple, effective, low-cost and eco-friendly manner.

Key Words: *ZnO NPs; VO2 NPs; WO3 NPs; Hydrothermal Synthesis; UV sensors; Biosensors;*

Acknowledgements: *This work was funded by the Project EXCL/CTM-NAN/0201/2012, the FEDER funds through the COMPETE 2020 Programme under the project UID/CTM/50025/2013.*

High performance field effect transistors based on single ZnO nanowires

C. FLORICA, A. Costas, E. Matei, A. Kuncser, N. Preda, I. Enculescu

National Institute of Materials Physics, Atomiştilor 405A, 077125 Măgurele – Ilfov, Romania

E-mail: camelia.florica@infim.ro

Building devices such as field effect transistors based on single semiconducting nanowires is an ongoing challenge due to their potential use in sensing or light emitting diode applications. Zinc oxide is an n-type semiconductor having a band gap around 3.3 eV and a large exciton binding energy of about 60 meV. ZnO nanowires can be grown using several methods such as electrochemical deposition, aqueous solution growth, thermal oxidation in air of zinc foils, etc.

The wet and dry preparation methods of ZnO nanowires govern their structural, morphological and optical properties (defect concentration, crystalline structure, roughness, etc.) and thus the performances of the build devices. We investigated how the properties generated by the growth techniques influence the performances of transistors based on single ZnO nanowires, this being crucial for their integration in applications. E-beam lithography was used to contact individual ZnO nanowires with Ti/Au ohmic electrodes in order to characterize them from the electrical point of view in the back gate transistor configuration using a SiO_2 layer as a gate dielectric. The influence of the bottom gate was considered and it was found that surface covering with a poly(methyl methacrylate) layer leads to improved transport properties for all the contacted ZnO nanowires due to surface passivation and gate coupling effects reduction.

The differences in the performances of the single ZnO nanowires based field effect transistors coming from the nanowires' preparation methods were evidenced and discussed. We achieved low power operation mode transistors with on-off current ratios up to 10^6, very high mobilities up to 147 cm^2/Vs, and switching behaviour better than those reported until now.

Selective exchange effects in single-Mn doped quantum dots

Radu DRAGOMIR

National Institute of Materials Physics, Atomiştilor 405A, 077125 Măgurele – Ilfov, Romania

E-mail: radu.dragomir@infim.ro

We calculate the exciton and biexciton structure in CdTe single-Mn doped cylindrical quantum dots with an embedded Mn atom. The position-dependent hole-Mn and electron-Mn exchange interaction affects the light-hole absorption spectrum and the exchange-induced Rabi oscillations of the excitonic populations. We predict that as the Mn atom approaches the cylinder edge the light-hole excitons are mixed by the hole-Mn exchange alone. We also investigated the dynamics of the mixed biexcitons and found hole-Mn exchange-induced Rabi oscillations of the biexcitonic populations for any location of the Mn atom on the z axis. As expected, these oscillations are damped by the intraband spin-conserving hole relaxation.

ULTRA-THIN and 2D

Electron spectromicroscopy of ferroelectric oxides

Nick BARRETT

SPEC, CEA, CNRS, Université Paris-Saclay, CEA Saclay 91191 Gif-sur-Yvette Cedex, France

E-mail: nick.barrett@cea.fr

Ferroelectric materials represent a potential technological breakthrough for post-CMOS electronics in terms of high density storage, rapidity, retention and energy consumption.

Non-invasive techniques are required to study the surface chemistry and electronic structure uynderlying their often unique electrical properties.

Advanced low energy electron optics has transformed photoelectron emission microscopy (PEEM) using synchrotron radiation and low energy electron microscopy (LEEM) into powerful techniques for the study of material surfaces. High lateral, wave-vector and energy resolution makes it possible to probe spatial variations in the chemical and electronic structure of nanoscale materials.

The principles of fully energy filtered PEEM and LEEM will be presented. By a combination of both direct and reciprocal space imaging the surface charge, work function, topography, chemistry and band structure can be studied. This will be illustrated by several examples.

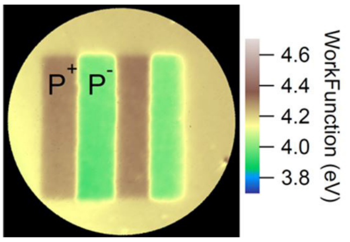
The surface charge and hence the ferroelectric (FE) polarization can be estimated from the surface potential and the work function as measured in LEEM and PEEM, respectively. There is a critical film thickness in $BiFeO_3$ below which the film polarization drops to zero despite constant tetragonality, suggesting the formation of stripe domains in ultra-thin films [1].

The band structure of ferroelectric domains in $BaTiO_3$(001) are studied using spatially resolved reciprocal space PEEM and synchrotron radiation. The dispersion relations can be correlated with domain chemistry and in- and out-of-plane ferrolectric polarization [2].

It is possible to switch the in-plane domain polarization using the electron beam of the LEEM. We show reversible switching using e-beam induced charge [3].

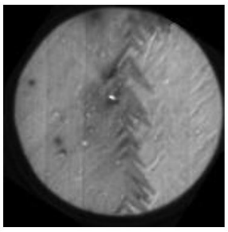
The phase transition in $BaTiO_3$ can be followed using LEEM revealing some fascinating kinetic domain ordering phenomena.

These examples demonstrate that the combination of real and reciprocal space imaging of ferroelectric surfaces using full field electron spectromicroscopy is a powerful new tool for unraveling the electronic structure underpinning ferroelectric order.

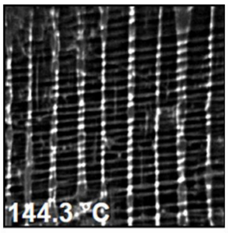


(a)

(b)



(b)



(d)

Figure (a) work function map of oppositely polarized FE domains in a 70 nm $BiFeO_3$ film. (b) energy cut in reciprocal space showing the twofold band structure symmetry in $BaTiO_3$ (c) electron beam induced switching in $BaTiO_3$ showing the characteristic advance of needle like cones across 90° domain walls. (d) Appearance of transitory strip domains during ferroelectric-paralectric phase transition in $BaTiO_3$.

[1] J. Rault, W. Ren, S. Prosandeev, S. Lisenkov, D. Sando, S. Fusil, M. Bibes, A. Barthélémy, L. Bellaiche and N. Barrett, Physical Review Letters 109, 267601 (2012)
[2] J. E. Rault, J. Dionot, C. Mathieu, V. Feyer, C. M. Schneider, G. Geneste, and N. Barrett, Physical Review Letters 111, 127602 (2013)
[3] J. E. Rault, T. O. Menteş, A. Locatelli, N. Barrett Scientific Reports 4, 6792 (2014)

Topological structures and torroidal ferroelectricity in ultra-thin films and devices

Marin ALEXE

Department of Physics, University of Warwick, Coventry, CV4 7AL, United Kingdom

E-mail: M.Alexe@warwick.ac.uk

It has been theoretically shown that in very thin and/or small systems the formation of ferroelectric domain walls is not energetically favourable. Instead vortex-type structure, involving polarization curling at unit cell, will form.[1,2] This has been recently shown at all scales, from macroscopic to medium range super-lattices. [3,4] While at the ferroelastic domain walls polarisation curling is highly probable due to perhaps to flexoelectric response to strain gradients, continuous polarization rotation at non-ferroelastic domain walls has been only seldom reported.[5,6]

Here we discuss occurrence and thickness dependence of topological at ferroelectric domain walls in capacitor-like Metal-Ferroelectric-Metal devices with ultra-thin, respectively 3, 6 and 9 unite cells (u.c.), $PbTiO_3$ films sandwiched between Co and $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) electrodes. As pointed recently, the present study might have implications in defining a new states of matter, such as dipolar skyrmions, in polar materials. The presence of these chiral topological states in bare capacitors opens the avenues in electrical control and local switching of chirality.

[1] I. Naumov, I. Bellaiche, and H. Fu, Nature (London) 432,737 (2004).
[2] M. G. Stachiotti and M. Sepliarsky, PRL 106, 137601 (2011)
[3] R. G. P. McQuaid et al., Nat. Commun. 2, 404 (2011)
[4] Y-L. Tang et al. Science 348, 547 (2015)
[5] C.-L. Jia, et al., Science 331, 1420–1423 (Mar. 2011)
[6] A. K. Yadav, et al, Nature doi:10.1038/nature16463 (2016)

Synchrotron radiation photoemission and photoelectron diffraction: the 2D materials case

Silvano LIZZIT

Elettra Sincrotrone Trieste, Italy

E-mail: silvano.lizzit@elettra.eu

In the last years the interest of the scientific community to graphene, the two-dimensional (2D) material composed by carbon atoms arranged in a honeycomb lattice, and also to other 2D atomic crystals such as hexagonal boron nitride (h-BN) or transition metal dichalcogenides (TMDCs), has literally exploded due to the very many unique properties that these materials possess. Many experimental and theoretical works have been performed, aimed to the synthesis and characterization of 2D materials. A wealth of experimental techniques, based on a surface science approach, have been used to perform these studies.

The talk will be dedicated to synchrotron radiation studies performed at the SuperESCA beamline of Elettra, the Italian synchrotron radiation facility, on 2D materials using high energy resolution X-ray photoemission spectroscopy (HR-XPS) and photoelectron diffraction (XPD). The XPS technique, used also in its fast modality to follow transient processes (Fast-XPS), and combined with theoretical modeling and complementary surface science techniques, is an extraordinary tool capable of exploring several aspects inherent to the chemistry and physics of materials in general, 2D atomic crystals in this specific case. The presentation should highlight the use and the information content obtained by exploiting these techniques.

Photoelectron spectromicroscopy of Pb(Zr,Ti)O_3(001) and (111) surfaces

Dana G. POPESCU, **Laura E. ABRAMIUC**

National Institute of Materials Physics, Atomiştilor 405A, 077125 Măgurele – Ilfov, Romania

E-mail: dana.popescu@infim.ro

Recently, photoelectron spectroscopy was validated as a valuable tool to derive band bending at free ferroelectric surfaces, intimately connected to the out-of-plane polarization state of the ferroelectric thin film [1-6]. The ability of photoelectron spectro-microscopy with sub-micrometre lateral resolution to identify ferroelectric domains by analysis of surface band bendings is demonstrated in this work on lead zirco-titanate (PZT), $PbTi_{0.8}Zr_{0.2}O_3$ thin films with (001) [7] and (111) [8] orientation, grown by pulsed laser deposition on corresponding $SrRuO_3/SrTiO_3$(001) or (111). Ferroelectric domains are visible as areas with different Pb 5d binding energy, attributed to different charge and polarization states of the film surface.

In the case of PZT(001), two novel effects are evidenced by using intense synchrotron radiation beam experiments on the order of 10^{11} photons / (s x μm^2): (i) the progressive increase of a low binding energy component for the Pb core levels (evidenced for both 5d and 4f, on two different measurement setups), which can be attributed to a partial decomposition of the PZT film at its surface and promoting the growth of metallic Pb during the photoemission process, with the eventuality of the progressive formation of areas with downwards ferroelectric polarization; (ii) for films annealed in oxygen in clean conditions (in an ultrahigh vacuum installation) a huge shift of the Pb 5d core levels (by 8-9 eV) towards higher binding energies is attributed to the formation of areas with depleted mobile charge carriers, whose surface density is insufficient to screen the depolarization field. This shift is attenuated progressively in time, as the sample is irradiated with high flux soft X-rays. The explanation of this evolution stems in the formation by photogenerated electron-hole pairs of charge sheets for compensation of the depolarization field. The initial formation of these areas with strong internal electric field promotes these films as good candidates for photocatalysis and solar cells, since in the operation of these devices the ability to perform charge separation and to avoid electron-hole recombination is crucial. Also, in such films the collection of charge carriers is likely to occur over the whole film thickness.

In the case of PZT(111), photoelectron spectromicroscopy evidenced shifts towards higher binding energy when the sample is subject to intense soft X-ray beam. A basic model is developed which supposes that photogenerated carriers reduce the depolarization field, yielding a lower torque applied to the ferroelectric polarization. As a consequence, the out-of-plane component of the polarization increases. Domain migration during irradiation with soft X-ray is inferred from the relative amplitude of the components with different binding energy. When the flux density of soft X-ray is on the order of 10^{11} photons / (s x μm^2), metal Pb clusters are formed at the surface on areas with the out-of-plane component of the polarization pointing outwards only.

References:

[1] Apostol, N.G., Stoflea, L.E., Lungu, G.A., Chirila, C., Trupina, L., Negrea, R.F., Ghica, C., Pintilie, L., Teodorescu, C.M., Appl. Surf. Sci. 273 (2013) 415-425.
[2] Apostol, N.G., Stoflea, L.E., Lungu, G.A., Tache, C.A., Popescu, D.G., Pintilie, L., Teodorescu, C.M., Mater. Sci. Eng. B 178, 1317-1322 (2013).
[3] Apostol, N.G., Stoflea, L.E., Lungu, G.A., Tanase, L.C., Chirila, C., Frunza, L., Pintilie, L., Teodorescu, C.M., Thin Solid Films 545 (2013) 13-21.
[4] Stoflea, L.E., Apostol, N.G., Chirila, C., Trupina, L., Negrea, R., Pintilie, L., Teodorescu, C.M., J. Mater. Sci. 49 (2014) 3337-3351.
[5] Ştoflea L.E., Apostol N.G., Trupină L., Teodorescu C.M., J. Mater. Chem. A 2 (2014) 14386-14392.
[6] Apostol, N.G., Ştoflea, L.E., Tănase, L.C., Bucur, I.C., Chirilă, C., Negrea, R.F., Teodorescu, C.M., Appl. Surf. Sci. 354 (2015) 459-468.
[7] Popescu, D.G., Huşanu, M.A., Trupină, L., Hrib, L., Pintilie, L., Barinov, A., Lizzit, S., Lacovig, P., Teodorescu, C.M., Phys. Chem. Chem. Phys 17 (2015) 509 - 520.
[8] Huşanu, M.A., Popescu, D.G., Tache, C.A., Apostol, N.G., Barinov, A., Lizzit, S., Lacovig, P., Teodorescu, C.M., Appl. Surf. Sci. 352 (2015) 73-81.

Synchrotron light for material characterization and modification in the framework of international projects

ANGELO AGOSTINO[1,3,4], Marco Truccato[2,4], Elisa Borfecchia[1,3], Lorenzo Mino[1,3], Valentina Bonino[1,2], Lise Pascale[1], Lorenza Operti[1,3,4], Natascia De Leo[5], Matteo Fretto[5], Gema Martinez-Criado[6] and Carlo Lamberti[1,3,4,7]

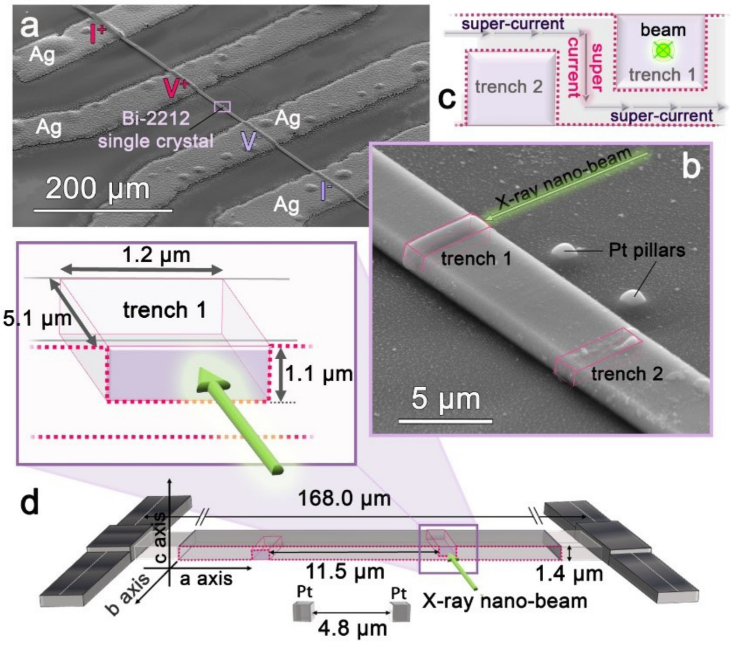
[1] *Department of Chemistry, University of Torino, via Giuria 7, I-10125 Torino, Italy*
[2] *Department of Physics, Interdepartmental Centre NIS, University of Torino, via Giuria 1, I-10125 Torino, Italy*
[3] *Interdepartmental Centre NIS and INSTM Centro di Riferimento, University of Torino, via Giuria 7, I-10125 Torino, Italy*
[4] *CrisDi Interdepartmental Center for Crystallography, University of Torino, via Giuria 7, I-10125 Torino, Italy*
[5] *INRIM, National Institute of Metrological Research, Strada delle Cacce 91, I-10135 Torino, Italy*
[6] *Experiments Division, European Synchrotron Radiation Facility, 6, rue Jules Horowitz, B.P. 220, F-38043 Grenoble Cedex, France*
[7] *Southern Federal University, Zorge Street 5, 344090 Rostov-on-Don, Russia*

E-mail: angelo.agostino@unito.it

This contribution aims to provide an overview of the potential of synchrotron-based X-ray techniques to elucidate the structural and electronic properties of advanced materials, and to track their evolution during chemically-relevant processes. Among them are for instance the well-established diffraction techniques and X-ray absorption spectroscopies (XAS), in both near (XANES) and post (EXAFS) edge regions.

Furthermore, a novel synchrotron-based X-ray nano-patterning technique able to fabricate electronic devices will be presented. In this contribution the production of a proof-of-concept device consisting of a few Josephson junctions produced by irradiating microcrystals of the $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi-2212) superconducting oxide with a 17.6 keV synchrotron nano-beam will be described. Fully functional devices have been obtained by locally turning the material into a non-superconducting state by means of hard X-ray exposure. Direct-write X-ray nano-patterning represents a promising fabrication method exploiting material/material rather than vacuum/material interfaces, with the potential for nanometric resolution, improved mechanical stability, enhanced depth of patterning and absence of chemical contamination with respect to traditional lithographic techniques.

Finally, it will be described how the increasing interest on synchrotron-based characterization and modification techniques, applied to advanced materials, can open new fields of research and offer strategical opportunities in order to attract European and international funds.



[1] M. Truccato et al., Nano Lett., 16 (3), 1669-1674 (2016)
[2] A. Pagliero et al., Nano Lett., 14, 1583–1589 (2014)
[3] W. Meevasana et al., Nature Mater., 10, 114-118 (2011)

ENERGY

Research on emerging materials for hybrid photovoltaics at Graz University of Technology

Thomas RATH

Institute for Chemistry and Technology of Materials (ICTM), Graz University of Technology, Stremayrgasse 9, 8010 Graz, Austria

E-mail: Thomas.rath@tugraz.at

The development of new materials and technologies for the supply of our society with clean energy is a very important and challenging field in today's materials science. In this talk current research activities on novel materials for hybrid solar cells at Graz University of Technology will be presented. Also our national and international collaborations in this research field and strategies for acquiring research projects will be discussed.

Our research focus is set on the development of novel synthesis strategies for nanomaterials and their application in hybrid solar cells, which are a very exciting solar cell technology as they combine beneficial properties of organic and inorganic semiconductors. They can take advantage of the high absorption coefficients and easy processability of organic materials as well as the superior electronic properties of inorganic semiconductors.

In recent years, we developed solution based in situ preparation routes for metal sulfide nanocrystals on mesoporous metal oxide scaffolds and directly in conjugated polymer films leading to ligand-free hybrid heterojunctions. Hybrid solar cells based on various metal sulfides (e.g. $CuInS_2$, CdS, SnS) and conjugated polymers have been successfully realized and studied in detail. A key issue in the further development of these in situ prepared hybrid solar cells is an improved control of materials synthesis, in particular, a good control over nanomorphology formation of polymer and nanocrystals in the absorber layer, which critically influences charge separation and also charge transport.

Our latest results obtained from a detailed study based on P3HT/CdS nanocrystal hybrid layers acting as a model material system disclose distinct influences of the precursor design on the absorber layer nanomorphology and also the solar cell performance. This comprehensive investigation of the formation of the nanomorphology during the in situ synthesis of the nanocrystals by time resolved grazing incidence small and wide angle X-ray scattering using synchrotron radiation as well as studying the influence of the nanomorphology on charge photogeneration by transient absorption spectroscopy was done together with our collaboration partners. The findings of this study provide a valuable tool for further research in the field of hybrid photovoltaics and will be used for the further optimization of hybrid solar cells based on non-toxic material combinations including Sb_2S_3, Bi_2S_3, SnS or $CuInS_2$ nanocrystals.

Ab initio calculations of the band alignment in halide perovskite solar cells

G. A. NEMNES (a), T. L. Mitran (a), Adela Nicolaev (a), Sorina Iftimie (a), L. Ion (a), S. Antohe (a),
N. Plugaru (b), C. Goehry (c), A. Manolescu (c)

(a) University of Bucharest, Faculty of Physics, Materials and Devices for Electronics and Optoelectronics Research Center, P.O. Box MG-11, 077125 Magurele-Ilfov, Romania
(b) Natl Inst Mat Phys, Magurele 077125, Ilfov, Romania
(c) School of Science and Engineering, Reykjavik University, Menntavegur 1, IS-101 Reykjavik, Iceland

E-mail: nemnes@solid.fizica.unibuc.ro

Hybrid lead-halide perovskite materials, in particular methylammonium lead halides of formula $CH_3NH_3PbX_3$ ($MAPbX_3$) with X = Cl, I, Br, have been in the focus of solar energy research for the past few years as prominent candidates for low-cost high-efficiency solar cells, with power conversion efficiencies (PCEs) steadily rising towards 21%. We investigate the band alignment at the interfaces between the halide perovskite and two different electron transport layers (ETLs), rutile-TiO_2 and Al-doped ZnO (AZO), by density functional theory calculations. We discuss the role of chlorine localized near the interface in the charge transfer for the case of the rutile-$TiO_2/MAPbI_{(3-x)}Cl_{(x)}$ interface [1]. As an alternative candidate to the more established TiO_2 based devices, ZnO has the benefit of larger electron mobility. However, the band alignment in the proximity of the $ZnO/MAPbI_3$ interface suggests the existence of spikes in both conduction and valence band edges, the former hindering the electron transfer into the oxide layer. By introducing Al doping, the bandgap of the interfacial AZO layer is shifted towards lower energies relative to the perovskite bandgap, eliminating the spikes in the band diagram [2]. This may be correlated with the observed experimental enhancement of the PCE for the AZO based devices.

[1] G. A. Nemnes, C. Goehry, T. L. Mitran, Adela Nicolaev, L. Ion, S. Antohe, N. Plugaru, A. Manolescu, "Band alignment and charge transfer in rutile-TiO2/CH3NH3PbI3-xClx interfaces", Phys. Chem. Chem. Phys. 17, 30417 (2015)
[2] Adela Nicolaev, T. L. Mitran, Sorina Iftimie, G. A. Nemnes, "Optimization of halide perovskite solar cells based on nanocolumnar ZnO", Sol. Energy Mater. Sol. Cells (doi:10.1016/j.solmat.2015.10.023, 2015)

New trends in directional solidification of multicrystalline silicon for photovoltaic applications

Daniel VIZMAN

Physics Faculty, West University of Timisoara, Bd. V. Parvan 4, 300223 Timisoara, Romania

E-mail: daniel.vizman@gmail.com

In the race to improve the price of solar energy by lowering the costs for silicon solar panel production, one of the important production segments to be addressed are the purification and crystallization of photovoltaic grade silicon. It stands for almost 1/3 of the total production cost. Currently, directionally solidified multi-crystalline silicon is predominant in the market of photovoltaic silicon (2015: 60%) and is expected to stay so during the following decade. This is mainly due to lower manufacturing costs and simpler process compared to Czochralski growth. The standard technology is based on the use of silica crucibles, coated with oxidized micrometer size Si_3N_4 grains to allow the detachment of the ingot after solidification and cooling to room temperature. Crystallization starts at the bottom of the crucible by lowering the temperature below the melting temperature. The thermal gradient is maintained by corresponding adjustments to the heater power. With the increasing demand for high efficient solar cells, one of the challenges in photovoltaic industry is the improvement in the quality of the silicon ingot during the solidification process. The properties of multicrystalline silicon, like minority carrier lifetime or diffusion length, which are key properties for the solar cell efficiency, are correlated to the content and the occurrence of C, N, O, metals and dopants as well as structural defects (dislocations, grain boundaries) and their interaction. The quality of the silicon ingot is strongly dependent on the growth parameters which control the melt flow and interface shape. On one hand a weak melt flow and a planar interface shape are favorable for a low level of thermal stress and dislocation density. On the other hand a stronger melt convection leads to a better mixing in the melt and thus is favorable to a homogeneous distribution of the impurities in crystal, but the purification efficiency also strongly depends on the solidification rate. In this view we proposed a configuration for melt stirring in DS using a type of electromagnetic field (EMF) [J. Cryst. Growth 318 (2011) 293; Eur. J. of mechanics B-Fluids, 52 (2015) 147]: the mould of rectangular shape is placed in a vertical magnetic field and an electrical DC current passes from the bottom of growing crystal to a small diameter electrode attached to the melt surface in the centre. The obtained numerical results showed indeed the stirring effect and indicated that the EMF generated vortex structure propagates very fast down to the solid-liquid interface which leads to a complete homogenization of the impurities in the melt after a short period of time.

As silicon is crystallized in non-reusable silica crucibles with anti-sticking silicon nitride coatings, research into alternative crucible materials is currently on-going. Several attempts have been made to develop reusable crucibles for silicon ingot crystallization, but all have failed to be introduced into the market. In this contribution, a comparison between the influences of two types of crucible material (quartz and graphite) and two coating materials (Si_3N_4 and $CaCl_2$) on the small diameter multicrystalline silicon ingots in a Bridgman-Stockbarger setup will be presented. The study focuses on the crystalline quality of the graphite crucible grown silicon ingots in respect to the standard quartz crucible grown ingots in similar conditions, for the different coating/crucible combinations. For this reason, primary issues such as the detachment from crucible, grain size and orientation and precipitate formation, will be addressed [J. of Crystal Growth, 401 (2014) 720-726].

Stability in perovskite solar cells

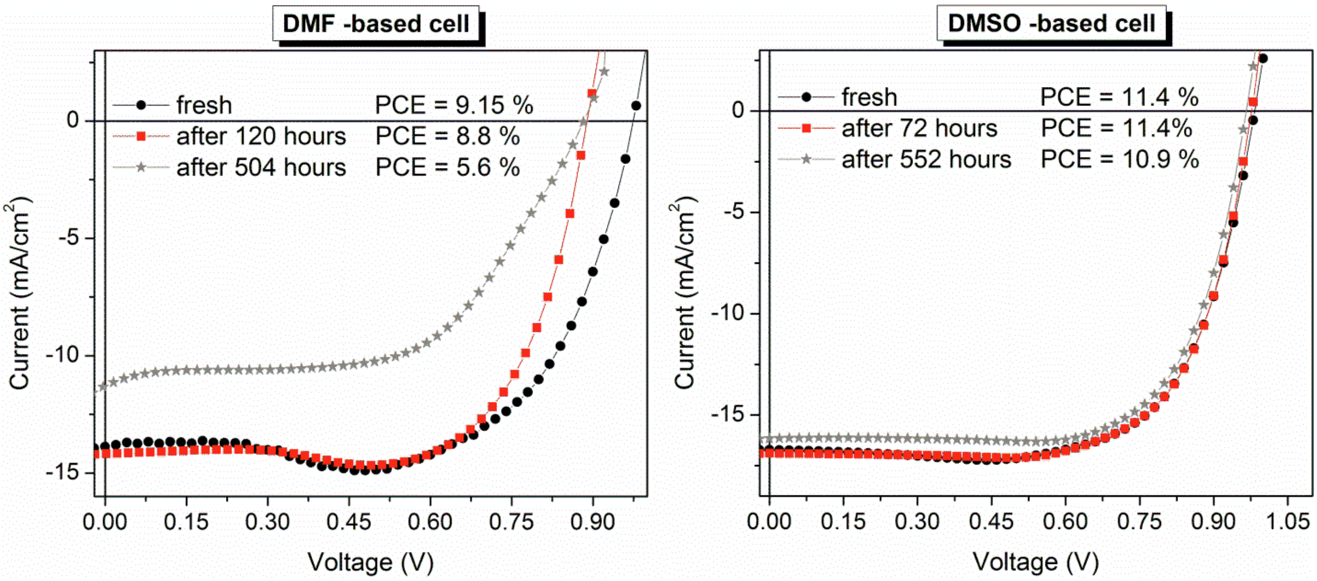
C. BESLEAGA[1], V. Stancu[1], A. G. Tomulescu[1], M. Sima[1], L. Stoflea[1,2], L. Pintilie[1], I. Pintilie[1]

[1] National Institute of Materials Physics, Romania
[2] Faculty of Physics, University of Bucharest, Romania

E-mail: cristina.besleaga@infim.ro

The hybrid perovskite ($CH_3NH_3MX_3$) exceptional attributes, including high carrier mobility, an adjustable spectral absorption range, and long diffusion lengths are the strengths of this "market-competitive" material for photovoltaic applications. The power conversion efficiency of the $CH_3NH_3MX_3$-based solar cells has reached 19% [1]. However, these devices are susceptible to chemical instability and then electrical degradation. Therefore, studies about their stability in time and reliability are mandatory in the search for new performance enhancement paths.

The present work reveals information about aging effects in perovskite photovoltaic devices with $CH_3NH_3PbI_3$ and $CH_3NH_3PbI_3$-xClx as active materials. The perovskite used here was synthesized by two chemical routes: using either dimethylformamide (DMF) or dimethylsulfoxide (DMSO) solvents. ence of the metallic top contact or chemical route for the perovskite fabrication is unveiled, and their effect on aging and device performance is discussed.



References:

[1] H. Zhou et al. , Science 345 (2014) 542

Atomistic simulations of methylammonium lead halide layers on $PbTiO_3$ (001) surfaces

N. PLUGARU,[1] G. A. Nemnes,[2] L. Filip,[1] , A. Manolescu[3], K. T. Butler,[4] L. Pintilie,[1] and I. Pintilie[1]

1. National Institute of Materials Physics, Atomistilor Str. 405A, Magurele-Bucharest, 077125, Ilfov, Romania.
2. Faculty of Physics, University of Bucharest, Atomistilor 405, Magurele-Bucharest, Ilfov, Romania.
3. School of Science and Engineering, Reykjavik University, Menntavegur 1, IS-101 Reykjavik, Iceland.
4. Centre of Sustainable Chemical Technology and Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, UK.

E-mail: plug@infim.ro

Recent investigations of hybrid perovskite (HP) solar cells have revealed that a significant increase in the solar energy conversion efficiency may be obtained in mixed halides $CH_3NH_3PbI_{3-x}Cl_x$ deposited on TiO_2 surfaces [1,2]. The partial chlorine substitution for iodine brings about chemical disorder, besides the structural one associated with the dynamics of the CH_3NH_3 molecule in the high temperature phases. The increased power conversion efficiency has been related to both modifications of charge density and carriers mobility in the chlorine substituted light absorber, as well as to particular effects at interfaces [3].

In this work we focus on the atomistic modeling and electronic properties of the 'pseudo-cubic' phase of $CH_3NH_3Pb(I,Cl)_3$ deposited on ferroelectric $PbTiO_3$ (PTO) (001) surface. We highlight the changes in the electronic states at the polarised interface, the band gaps, band alignment, and charge densities, in relationship with Cl concentration and distribution, as well as the PTO surface termination. The effect of the PTO polarisation direction on the planar and macroscopic averages of the Hartree potential along the z-axis of the heterostructures is also discussed (see the Figure for an illustrative example). Significant consequences of the charge density variation with Cl distribution in the HP layer, on the potential variation across the interface, are derived. The present results are discussed in comparison with those obtained for systems with the HP layer deposited on TiO_2 substrates.

[1] H. S. Jung and N.-G. Park, Small 11, 10 (2015).
[2] S. Colella et al., J. Phys. Chem. Lett., 5, 3532 (2014).
[3] G. A. Nemnes et al., Phys. Chem. Chem. Phys., 17, 30417 (2015).

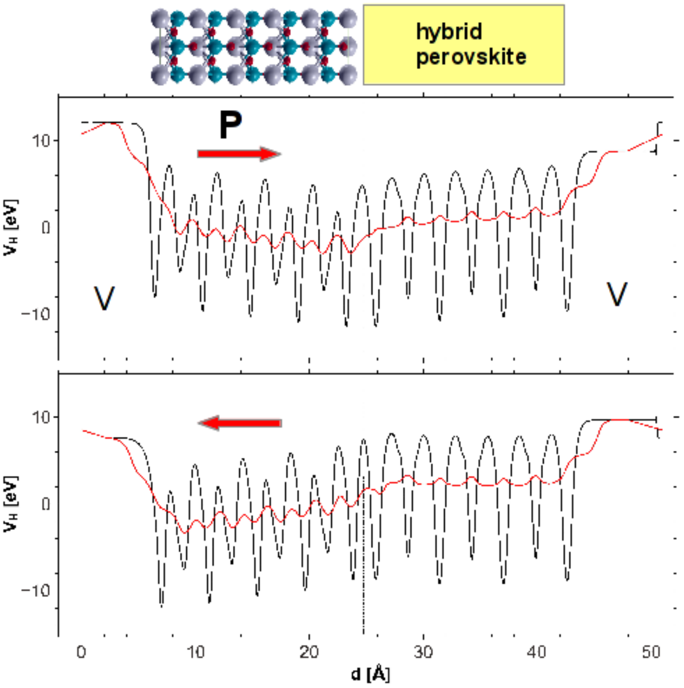


Figure. Illustrative plots of the planar (black) and macroscopic (red) averages of the Hartree potential, VH, along the z-axis of a model heterostructure. The polarisation, P, direction in the $PbTiO_3$ layer has an obvious effect on the shape of the potential at the interface as well as the ionization potential value.

MATERIALS FOR LIFE SCIENCES, CATALYSIS

Nanoparticles for multimodal clinical and preclinical in vivo imaging

Mangala SRINIVAS

Dept. of Tumor Immunology, Radboud University Medical Centre, Radboud University, Nijmegen, The Netherlands

E-mail: Mangala.Srinivas@radboudumc.nl

Modern medicine is all about personalisation- whether in cell therapy, targeted delivery or even patient stratification. These require noninvasive techniques to monitor relevant issues in vivo. Imaging is a key player in this field. Although several imaging modalities are available, none are ideal. Thus, my group is focusing on the development of multimodal imaging agents for a range of applications. In particular, we are working with nanoparticles designed for 19F MRI, fluorescence, ultrasound and optoacoustic imaging. These agents have been approved for clinical testing, where late-stage melanoma patients will receive therapeutic dendritic cells pre-labeled with the nanoparticles for imaging. The data obtained will help us optimise and customise this therapy for our patients. Furthermore, we are also working on understanding the physical structure of these unique nanoparticles, as well as exploring a range of relevant biological applications.

Low T_C Glassy Magnetic Alloys for Medical Applications

Nicoleta LUPU

National Institute of Research and Development for Technical Physics, Iasi, Romania

E-mail: nicole@phys-iasi.ro

The need for curing various incurable diseases is demanding not only new types of materials, which preferably will mimic the nature functionalities, but also the understanding of their properties in relation with their microstructure. In this context, the use of magnetic hyperthermia for curing cancer appears to be an extremely viable one. Fe oxides nanoparticles with superparamagnetic behavior (SPIONs) are extensively used in clinical tests involving magnetic hyperthermia. Among the concerns about SPIONs use in magnetic hyperthermia tests, one should mention: the preservation of the stability of Fe oxide NPs against oxidation, the limitations imposed to stop the heating of Fe-oxides (mainly Fe_3O_4) at moderate temperatures (below 470 °C), and, most importantly, the capacity to retain the temperature in the range of 41-460 °C, which requires a very rigorous control of the power of the high frequency generator.

To overcome these issues, we have developed a new type of ferromagnetic nanoparticles (the saturation magnetization is higher compared with Fe-oxides and the hysteresis losses are reduced as well), with the nominal compositions $Fe_{79.7-x}ETM_xNb_{0.3}B_{20}$ (ETM = Cr, Ti, Ta, Mn; x = 12÷20 at.%), with low Curie temperatures compared with SPIONs, which can be tailored easily and precisely in the 0÷700 °C by modifying the ETM content, with an accuracy of less than 10°C, more suitable for self-regulating magnetic hyperthermia. The purpose of the present study was to evaluate in vitro the cytotoxicity of $Fe_{79.7-x}ETM_xNb_{0.3}B_{20}$ alloy nanoparticles, coated or not by a biocompatible layer. The effect of Fe-ETM-Nb-B magnetic nanoparticles on tumor cells (human osteosarcoma cancer cells) was investigated prior and following particle activation by an a.c. electromagnetic field of 350 mT (f = 153 kHz) created by a home-made magnetic-induction hyperthermia unit.

This work was financially supported by the UEFISCDI grant #148/2012 (HYPERTHERMIA).

Dental implant fixtures bio-functionalized with mechanically resistant and cytocompatible bioglass coatings by magnetron sputtering technique

G.E. STAN [1,*], A.C. Popa[1,2], M.A. Husanu[1], M. Enculescu[1], C. Tanase[3], J.M.F. Ferreira[4]

[1] *National Institute of Materials Physics, 077125 Magurele, Romania*
[2] *Army Centre for Medical Research, 020012 Bucharest, Romania*
[3] *"Victor Babes" National Institute of Pathology, 050096 Bucharest, Romania*
[4] *Department of Materials and Ceramics Engineering, CICECO, University of Aveiro, 3810–193 Aveiro, Portugal*

E-mail: george_stan@infim.ro

Bioactive glasses (BG) are osteoproductive-type inorganic materials possessing the highest indices of bioactivity, and are currently considered as the suitable candidates to stir the quest for a new generation of osseous implants with superior biological/functional performance. An exploratory magnetron sputtering (MS) study was employed in the search of the deposition variables capable to imprint suitable chemical, structural, mechanical, and biological properties to the coatings. The prerequisites for reliable implant-type coatings are both their biological and mechanical performances. In congruence with this vision, this contribution introduces for the first time a reliable technological recipe for coating fairly complex 3D-shaped dental implants with uniform and mechanical resistant BG coatings by the MS method. The mechanical reliability of the BG coatings applied to real Ti dental implant fixtures has been evaluated by a procedure comprised of "cold" implantation in pig mandibular bone from a dead animal, followed by immediate tension-free extraction tests. The effects of the complex mechanical strains occurring during implantation were analysed by SEM-EDS. Extensive biocompatibility assays (MTS, immunofluorescence, Western blot) revealed that the BG coatings stimulated strong cellular adhesion and proliferation of human dental pulp stem cells, without promoting their differentiation. The ability of the BG implant coatings synthesized by MS to conserve a healthy stem cell pool is promising to further endorse the fabrication of new osseointegration implant designs with extended lifetime.

Nanoparticles and nanoclusters versatile synthesis methods: pathway towards integrated devices for nanosensing and biomedical applications

Ovidiu CRISAN

National Institute of Materials Physics, Atomiştilor 405A, 077125 Măgurele – Ilfov, Romania

E-mail: ocrisan@infim.ro

Complementary methods of synthesis of magnetic nanoparticles and nanoclusters, namely the cluster aggregation method and the laser pyrolysis method, are presented and systems obtained using these methods are shown to be promising in view of potential biomedical applications and hybrid integration into devices with nanosensing capabilities.

A versatile method of synthesis of cluster-assembled magnetic nanoparticles is presented and the properties of the obtained gas-stabilised surface-functionalized Fe oxide clusters are reported. The technique uses Ar gas flow which captures evaporated metal vapours and sputters the condensed clusters in-situ onto suitable chosen substrates into a home made UHV chamber connected to a multiple cluster source. Extremely rigorous control of the size distribution and cluster density is achieved. Cluster size is controlled by the vapor pressure of the metal source inside the pick-up chamber. Detailed analysis of the TEM micrographs of the Fe oxide clusters onto C coated Cu grids shows that there is a simple linear relationship between average metal cluster size and metal vapor pressure during deposition. Magnetic properties are investigated and correlated with the cluster structure. Enhanced coercivity is observed for the Fe clusters and attributed to strong planar magnetic anisotropy induced during gas exposure. Initial promising results towards biomedical applications are presented.

A novel hybrid magnetic-semiconductor structure obtained from magnetic core-shell nanoparticles deposited onto prepatterned Si (111) substrate with basic logic circuitry made of metallic conductive lines is created and its capabilities are demonstrated in terms of magnetotransport properties. The laser pyrolysis method is employed in order to synthesize magnetic core-shell Fe / FeC nanoparticles with sizes between 12 – 15 nm. E-beam lithography has been used in order to design and execute two different layouts of prepatterning with logic capacity, one with two pads and 50 microns thick conductive metallic lines, another one with 4 pads and parallel 5 microns thick conductive lines separated by 5 microns thick spacer. The as-obtained structures are morphologically characterized by means of optical, scanning and transmission electron microscopies. As-synthesized core-shell nanoparticles have been magnetically characterized inasmuch as the hybrid device obtained by depositing centrifugated and dispersed core-shell nanoparticles from liquid carrier solutions. For the first time, a significant giant magnetoresistive (GMR) effect has been observed and measured for the hybrid architectured device Fe / FeC nanoparticles on pre-patterned Si (111) substrate. A ΔR/R of 6% at 4.2 K has been measured from conductivity-in-plane electron transport measurements. This opens possibilities for the use of such devices as magnetic GMR-based sensors.

LARGE INFRASTRUCTURES

SLONMR: From small organic compounds to macromolecules

Primož ŠKET[1,2], Janez Plavec[1,2,3]

1 Slovenian NMR Centre, National Institute of Chemistry, Hajdrihova 19, SI-1001, Ljubljana, Slovenia
2 EN-FIST Centre of Excellence, Trg OF 13, SI-1001, Ljubljana, Slovenia
3 Faculty of Chemistry and Chemical Technology, University of Ljubljana, Večna pot 113, SI-1000 Ljubljana, Slovenia

E-mail: primoz.sket@ki.si

Slovenian NMR centre (SLONMR) is a national facility and organizational unit within National Institute of Chemistry (NIC) that offers infrastructure and expertise in the field of NMR spectroscopy to scientists and researchers in academic and industrial institutions. NMR spectroscopy is method which allows the study of the correlations between the structure of materials of biological or other origins, as well as explores their dynamics and molecular recognition. NMR is thus a key to gaining insight into the biological functions, chemical structure, and interactions of molecules in both the liquid and solids. Therefore it can be used to gain insight into the nature of the fundamental processes which underlie the production and development of different preparations.

In particular, we are studying interactions of anionic ligands with receptors. We can establish conformational preferences of these molecules before and after interaction with various anions by the use of NMR spectroscopy in liquid state. These structural features are essential for further development of anionic ligands used as anionic transporters. Additionally, we are experts in the determination of nucleic acid structures (DNA and RNA) and their interactions in solution. Extensive part of our research includes characterization of protein structures and their dynamics in solution. We are also involved in characterization of pharmaceutical products in liquid as well as in solid state. Solid state NMR is also used for studies of porous materials including zeolites and metal-organic framework materials in order to determine their structures, to understand the performance of these materials in the fields of energy storage and gas separation and storage.

SOLARIS – New European light source

Marek STANKIEWICZ

National Synchrotron Radiation Centre SOLARIS
Uniwersytet Jagiellonski ul. Czerwone Maki 98 30-392 Kraków

E-mail: m.j.stankiewicz@uj.edu.pl

The new synchrotron light source SOLARIS has been constructed in Kraków, Poland. The project is the result of the long term efforts of building the first synchrotron radiation facility in Poland. It addressed the expectation of Polish research community. The idea of its creation has been supported by the strong community of few hundred Polish synchrotron radiation users, who for years have been collaborating with synchrotron facilities abroad. 34 Polish research institutes and universities which were interested in applying synchrotron radiation to their research created the Synchrotron Radiation Consortium. The final application formulated by the Jagiellonian University initiative group for construction of the National Synchrotron Radiation Centre in Kraków was submitted in 2009 and the project was granted execution by the Jagiellonian University in March 2010. The project was funded from the EU Structural Funds – European Regional Development Fund within the frame of the Innovative Economy Operational Program (no: POIG.02.01.00-12-213/09). At the end of 2015 the project was completed and National Synchrotron Radiation Centre SOLARIS at the Jagiellonian University was created. The facility is situated within Kraków borders, at the Jagiellonian University III Campus area, the new location for the Science Faculties and the site of the Jagiellonian Centre of Innovation – the Life Science Park. The total project budget was approx. 49 MEUR.

The primary project objective was to construct possibly the best, state of the art, medium energy synchrotron radiation source. This challenge was resolved due to the very advantageous correlation with the MAX-IV project which came about at the same time in Sweden. MAX-IV is replacing the 30 years old Max-Lab – national Swedish synchrotron radiation source in Lund by the new facility consisting of two synchrotrons with 1.5 and 3.0 GeV energy. The design of these new synchrotrons is based on revolutionary idea of constructing electromagnetic bending cells in one piece of iron. This solution provides exceptional quality of the photon beam and has the big economical aspect. As a result of the unprecedented collaboration with the MAX-lab management and the team, SOLARIS was allowed to utilized the design of the smaller MAX-IV synchrotron . The 96m circumference, 1.5GeV, 500 mA synchrotron storage ring with the critical energy of the bending magnet radiation spectrum at approx. 2 keV, with the emittance of less than 6 nm rad. SOLARIS will deliver radiation from the bending magnets and insertion devices is in the range from IR to hard X-rays offering research opportunities in diverse fields of research.

It has to be acknowledged that construction of SOLARIS within such a short time and very limited budget would not be possible without the very appreciated collaboration with many synchrotron radiation facilities worldwide. MAX-lab has to be particularly acknowledged as the source of the unmatched expertise and competence. Sincrotrone ELETTRA in Trieste has also to be pointed out for providing know how for SOLARIS in many

The project was officially completed in December 2015. During the project the following planned major deliverables have been achieved:

- Building (approx. 8000 m^2 internal area)
- injector (linear accelerator) – six S band 3 GHz accelerating sections delivering 0.6 GeV final energy
- 96 m circumference 12 fold symmetry storage ring of 500mA 1.5 GeV electrons
- two experimental beamlines with 3 experimental stations: PEEM, XAS, UARPES

Chemistry of carbon and carbon monoxide on Pb(Zr,Ti)O$_3$(001) surfaces

Nicoleta G. APOSTOL

National Institute of Materials Physics, Atomiştilor 405A, 077125 Măgurele – Ilfov, Romania

E-mail: nicoleta.apostol@infim.ro

Ferroelectric materials, known also for several decades for their good piezoelectric and pyroelectric properties, are nowadays reconsidered in view of their possible active role in catalysis [1] and in photocatalysis [2]. The reasons for these applications are (a) the ability of a charged surface to trap polar molecules [3,4], which is pre-requisite for catalytic processes; (b) the active role of the surface field of the ferroelectric, able to induce molecular dissociations in some cases. Thus, catalytic activities might be triggered by controlling the ferroelectric polarization [5]. Photocatalysis on ferroelectric semiconductors benefits also from the existence of built-in electric fields at the surface, for electron-hole separation, with direct impact on lowering of the recombination rate [6]. Understanding and quantifying these phenomena needs to work on model systems, such as ferroelectric thin films with well-defined crystal structure, single orientation and uniform polarization. Such samples have been possible to prepare only for the last few years by pulsed laser deposition (PLD) [8-15], and only very recently such samples could be re-processed in ultrahigh vacuum (UHV), yielding single crystal layers with undetectable contamination and well defined structure, as shown by clear low energy electron diffraction (LEED) patterns.

We will discuss results involving carbon monoxide adsorption and carbon deposition using surface science methods (performed in UHV) involving ferroelectric lead zirco-titanate (PZT) thin films grown by PLD on single crystal $SrRuO_3$./$SrTiO_3$(001) or Pt(001) substrates. Surface science sample treatment and analyses (photoemission and LEED) are performed in UHV (low 10-10 mbar), by two UHV setups installed on the SuperESCA beamline at the Elettra synchrotron in Trieste, Italy. The stabilization of out-of-plane polarization was found to be strongly dependent on the inherent creation of intrinsic defects in the ferroelectric layer [14], in order to provide charge carriers able to screen the depolarization field. Most films exhibit outwards, P(+) polarization; however, ultraclean films with near-perfect stoichiometry $PbTi_{0.8}Zr_{0.2}O_3$(001) exhibit inwards polarization, P(-). Only these surfaces were able to absorb CO molecules in relevant quantities onto them (but still below a single atomic layer). By warming the films above the Curie temperature, the polarization vanishes, CO is desorbed and the surface layers are depleted in oxygen, which is a sign of CO oxidation. When carbon is deposited, we noticed reversible Pb migration inside the layers. Carbon deposition proceeds to the formation of two-dimensional layers with a weak chemical interaction with the substrate, exhibiting mostly sp2 bonding up to carbon surface densities similar to that of graphene. All these features promote ferroelectric thin films as valuable candidates for a wide range of applications in triggering chemical processes or graphene synthesis on their surfaces.

[1] Garrity, K., Kolpak, A.M., Ismail-Beigi, S., Altman, E.I., Adv. Mater. 22 (2010) 2969-2973.

[2] Li, L., Salvador, P.A., Rohrer, G.S., Nanoscale 6 (2014) 24-42.

[3] Li, D.G., Zhao, M.H., Garra, J., Kolpak, A.M., Rappe, A.M., Bonnell, D.A., Vohs, J.M., Nature Mater. 7 (2008) 473-477.

[4] Ştoflea L.E., Apostol N.G., Trupină L., Teodorescu C.M., J. Mater. Chem. A 2 (2014) 14386-14392.

[5] Yun, Y., Altman, E.I., J. Am. Chem. Soc. 129 (2007) 15684-15689.

[6] Cui, Y.F., Briscoe, J., Dunn, S., Chem. Mater. 25 (2013) 4215-4223.

[7] Galca, A.C., Stancu, V., Husanu, M.A., Dragoi, C., Gheorghe, N.G., Trupina, L., Enculescu, M., Vasile, E., Appl. Surf. Sci. 257 (2011) 5938-5943.

[8] Apostol, N.G., Stoflea, L.E., Lungu, G.A., Chirila, C., Trupina, L., Negrea, R.F., Ghica, C., Pintilie, L., Teodorescu, C.M., Appl. Surf. Sci. 273 (2013) 415-425.

[9] Apostol, N.G., Stoflea, L.E., Lungu, G.A., Tache, C.A., Popescu, D.G., Pintilie, L., Teodorescu, C.M., Mater. Sci. Eng. B 178, 1317-1322 (2013).

[10] Apostol, N.G., Stoflea, L.E., Lungu, G.A., Tanase, L.C., Chirila, C., Frunza, L., Pintilie, L., Teodorescu, C.M., Thin Solid Films 545 (2013) 13-21.

[11] Stoflea, L.E., Apostol, N.G., Chirila, C., Trupina, L., Negrea, R., Pintilie, L., Teodorescu, C.M., J. Mater. Sci. 49 (2014) 3337-3351.

[12] Apostol, N.G., Ştoflea, L.E., Tănase, L.C., Bucur, I.C., Chirilă, C., Negrea, R.F., Teodorescu, C.M., Appl. Surf. Sci. 354 (2015) 459-468.

[13] Pintilie, I., Teodorescu, C.M., Ghica, C., Chirila, C., Boni, A.G., Hrib, L., Pasuk, I., Negrea, R., Apostol, N.G., Pintilie, L., ACS Appl. Mater. Interf. 6 (2014) 2929-2939.

[14] Pintilie, L., Ghica, C., Teodorescu, C.M., Pintilie, I., Chirila, C., Pasuk, I., Trupina, L., Hrib, L., Boni, A.G., Apostol, N.G., Abramiuc, L.E., Negrea, R., Stefan, M., Ghica, D., Sci. Rep. 5 (2015) 14974(1-14).

[15] Popescu, D.G., Huşanu, M.A., Trupină, L., Hrib, L., Pintilie, L., Barinov, A., Lizzit, S., Lacovig, P., Teodorescu, C.M., Phys. Chem. Chem. Phys 17 (2015) 509 - 520.

Electron microscopy at NIMP: capabilities and collaboration opportunities

Raluca NEGREA

National Institute of Materials Physics, Atomiştilor 405A, 077125 Măgurele – Ilfov, Romania

E-mail: raluca.damian@infim.ro

High-Resolution Analytical Transmission Electron Microscopy represents nowadays one of the most powerful tools in microstructural characterization of advanced materials.

At NIMP we have developed a highly equipped laboratory of electron microscopy including three transmission electron microscopes dedicated to different TEM techniques, one SEM-FIB dual system for thin lamella preparation and morphological/compositional investigations as well as a laboratory provided with various techniques for TEM/SEM specimen preparation.

The electron microscopy facilities installed at NIMP have been included in the Central European Research Infrastructure Consortium along with complementary research equipments in the field of materials and biomaterials from 8 other Central European countries.

This talk will shortly present the microstructural investigation capabilities of the TEM facilities available at NIMP, illustrated by a series of results obtained in the frame of the national research projects as well as within CERIC.

CERIC-ERIC - European Research Infrastructure Consortia and Materials Science in Central East Europe

Jana KOLAR

CERIC-ERIC, S.S. 14 – km163.5, 34149 Basovizza (TS), Italy

E-mail: jana.kolar@ceric-eric.eu

Material science and nanotechnology are two of the main research fields to take up future challenges of Europe such as alternative energy sources and energy storage or biomedical and pharmaceutical materials. The scientific problems coming up in this fields have become more and more complex in the recent years and require an ever increasing number of instrumental and analytical techniques and disciplines. Such complexity requires the availability of expertise as well as open access to a wide range of probing techniques and many different complementary instruments.

The CERIC-ERIC research infrastructure was developed to face this challenge and to make a wide variety of instruments distributed across central and eastern Europe available through free open access. It comprises synchrotron radiation, neutron radiation, microscopic techniques, ion-beam analysis methods and NMR. The selection of proposals and experiment time is done in a peer-review process and based on scientific excellence only. Following the nature of CERIC as a multi-probe facility, the open access operation allows to ask not only one instrument per proposal but to get experiment time granted for several complementary instruments with one proposal.

The talk will present CERIC, its structure and scientific focus. It will further highlight CERICs opportunities for researchers as well as the possibilities to act as a versatile and strong partner.

Keywords: *Research Infrastructure, multi-technique research, synchrotron radiation, material science, nano analytics*

FUNCTIONALITIES

Long range symmetry propagation initiated at heterostructure interfaces

Guus RIJNDERS

MESA$^+$ Institute for Nanotechnology, University of Twente, P.O.BOX 217, 7500 AE, Enschede, The Netherlands

E-mail: a.j.h.m.rijnders@utwente.nl

Diverse electronic phases in complex oxide materials such as superconductivity, magnetic phases and ferroelectricity are intimately coupled to the crystal symmetry. Atomic layer controlled growth of oxide heterostructures offers a flexible route to tune the symmetry and this has been shown to give rise to many unusual emergent properties that are absent in the original materials. Using such atomic layered growth, we have fabricated perovskite heterostructures in which the altered symmetry is found to propagate over a long range. The interfacial octahedral coupling induced symmetry can even propagate throughout the total thickness of epitaxial films. Desired symmetries of perovskite heterostructures are furthermore achieved by engineering the substrate symmetry, for example by introducing a buffer layer with different symmetry. Our results demonstrate that the long range symmetry propagation can effectively control metal to insulator transition, as well as magnetic ordering.

In this contribution, I will focus on the fabrication of epitaxial heterostructures, the analysis of the crystal symmetry using x-ray diffraction, and high-resolution STEM, as well as resulting properties of magnetic phases.

Keywords: *Oxide Heterostructures, Interfacial Reconstruction.*

Hard Magnetic Materials with Reduced Rare-Earth Content

Viorel POP

Faculty of Physics, Babes-Bolyai University, 3400 Cluj-Napoca, Romania

E-mail: viorel.pop@phys.ubbcluj.ro

Permanent magnets as well as the easy controllable magnetic materials are crucial components in both ubiquitous devices and advanced technologies, being therefore of high importance for current industries and future developments. Of all the magnets on the market, the rare earth (RE) based permanent magnets present the best magnetic properties. The major weakness of RE based magnets consists in the global distribution of rare earths, a significant percentage of deposits being located in China, which resulted in a high price and high risk of these materials. This contribution aims to present our research on new magnetic materials for the next generation of RE lean (or free) permanent magnets, more precisely on rare-earth free magnetic materials (Mn-Al or Mn-Bi) and exchange-spring nanocomposite magnets. Nanocrystalline/nanocomposite exchange-spring magnets are formed of soft and hard magnetic phases dispersed on the nanometer scale and coupled by exchange interaction. The interphase exchange coupling is strongly influenced by the microstructure. Our studies include the search for the optimum interphase coupling in hard-soft nanocomposites. These composites are made by co-milling of hard magnetic phase- powders ($SmCo_5$ or $R_2Fe_{14}B$) with Fe or Fe-based alloys powders. The structure and microstructure of milled composite were tailored by different heat treatments. Another direction of our researches is focused on new promising magnetic phases, without rare earths, with high coercivity and interesting magnetic properties as Mn-Bi or Mn-Al intermetallic phases. The samples are obtained by induction or arc melting. The increase of the saturation magnetisation and the stability of the ferromagnetic phases are monitored by different heat treatments or small substitutions in the alloys' composition.

The structural evolution was followed by X-ray diffraction, DSC measurements, Mössbauer spectrometry and electron microscopy. The coercive field, remanence and the degree of hard/soft exchange coupling were studied from hysteresis cycle measurements in magnetic fields up to 12 T and dM/dH vs. H curves.

In my presentation, I will also give some information on the major research subjects of our laboratory and on the main scientific collaboration: Technical University of Cluj-Napoca, National Institute of Materials Physics Bucharest, Université Grenoble Alpes, Institut Néel, Université de Rouen etc.

Thin film catalysts for fuel cell technology

Vladimír MATOLÍN [a,b]

a)Charles University in Prague, Faculty of Mathematics and Physics, V Holešovičkách 2, 18000 Prague 8, Czech Republic
b)CERIC SPL-MSB partner facility

E-mail: matolin@mbox.troja.mff.cuni.cz

Preparation of catalysts using thin film techniques is not used yet in heterogeneous catalysis because TF technologies are generally considered as incompatible with the preparation of sufficiently large surface areas. Moreover catalytic loading of large-sized reactors is not possible. These arguments, however, do not hold for the proton exchange membrane fuel cell application. The thin-film coating technology for supported catalysts can be parallelized and scaled, with the size of the deposition facility being the only limitation. Most importantly, however, high-surface-area nanoporous catalyst films can indeed be prepared by suitable deposition techniques.

Platinum is the most versatile element in catalysis, but it is rare and its high price limits large-scale applications, for example in fuel cell technology. Still, conventional catalysts use only a small fraction of the Pt content, i.e. those atoms located at the catalyst's surface.

Deposition of very thin films of Pt on nanoporous carbon-ionomer-layers which are composed of conductive nanoparticles interconnected by nafion+PTFE bridges makes possible to prepare highly dispersed catalysts ensuring high fuel cell activity at very low Pt loading. To maximize the noble metal efficiency, we can go even further by preparing atomically dispersed Pt is a suitable matrix. One example is ionic Pt anchored at specific sites of cerium oxide surfaces.

AC driven magnetic flux quanta in YBCO composite thin films with complex pinning structures

I. IVAN[1], P. Mele[2], D. Miu[3], and L. Miu[1]

[1] National Institute of Materials Physics, 77125 Bucharest-Magurele, Romania
[2] Hiroshima University, Institute for Sustainable Sciences and Development, 739-8530 Higashi-Hiroshima, Japan
[3] National Institute of Laser, Plasma, and Radiation Physics, 77125 Bucharest-Magurele, Romania

E-mail: john007buc@yahoo.com

The complex ac susceptibility $\chi=\chi'-i\chi''$ of YBCO composite thin films with strong pinning centers ($BaZrO_3$ nanorods and added Y_2O_3 nanoparticles), has been studied as a function of temperature, driving field amplitude and ac frequency at 0.2, 1 and 3 T static magnetic fields. The current dependence of the activation energy U is derived in the framework of thermally activated hopping of vortices over pinning potential, yielding a logarithmic U(J) dependence. Results show unexpected high values of U of the order of 103 K close to the irreversibility line.

Photoinduced carrier dynamics – the ferroelectric dipole's influence on recombination

Steve DUNN

School of Engineering and Materials Science,Queen Mary University of London

E-mail: s.c.dunn@qmul.ac.uk

There has been growing interest in the use for non-centrosymmetric systems for a wide range of energy harvesting applications which include kinetic to electric and photonic to chemical or electric. Recently there has been interest in using a ferroelectric material as a photocatalyst where the domain structure determines band structure and dictates the redox chemistry at an interface. We recently showed the photocatalytic performance of $BaTiO_3$ can is enhanced to match that of TiO_2 by depositing nanostructured silver 5. However, most published work has not investigated the photophysics and photoinduced carrier dynamics. In this work we use transient absorption spectroscopy to probe the influence of crystallographic orientation on carrier dynamics for a range of $BaTiO_3$ single crystal substrates. We extend our study to investigate the influence of temperature on carrier dynamics by testing the $BaTiO_3$ below and through the Curie temperature. Our results show that $BaTiO_3$ has a carrier lifetime that exceeds 1 second at room temperature under no external field. This exceeds the measured values for Fe_2O_3 when an applied bias of 1V (versus the reversible hydrogen electrode) is present. This finding indicates that the internal dipole of the ferroelectric has a significant impact on the recombination rate of photoinduced carriers. Furthermore, our data presents a thermal trend that is fully consistent with changes in the crystal structure and associated changes in dielectric constant and remnant polarization. When $BaTiO_3$ of different crystallographic orientations are investigated we see a trend in relaxation times consistent with the orientation of the polar dipole. At temperatures above the Curie point the $BaTiO_3$ samples show an extended tail of recombination that is closely matched across all samples; we believe this is due to the high density of trap states in the system. However, below the Curie point there are significant differences in the shape of the decay profile. We explain these differences by relating the crystal structure of the exposed face and influence of dipole on recombination profiles for the excited carriers. In summary, we have investigated the photophysics of $BaTiO_3$ single crystals showing remarkable long lived photogenerated charge carrier with a crystal orientation, and temperature, dependency on lifetime and decay mechanisms of the electron hole pair.

Research in Materials Physics at Ovidius University of Constanta

Mihai A. GIRTU

Department of Physics and Electronics, Ovidius University of Constanța, Constanța 900527, Romania

E-mail: mihai.girtu@univ-ovidius.ro

Ovidius University of Constanța is a public higher education institution, which was founded in 1961 and became a comprehensive university in 1990. With over 15000 students in bachelor's, master's and doctoral programs, of which over 1200 international, Ovidius is the largest university at the Black Sea in the European Union. As the fields of study in which the university offers degrees are very diverse, from medical and life sciences to engineering, from natural sciences to humanities, from social and economic sciences to arts and theology, the research interests are equally diverse.

An important role in the research endeavors of the university is played by materials physics, with applications in energy production, environmental protection, photocatalysis, medicine, pharmacy and biotechnologies. Some examples of research accomplishments by various research groups active in these fields are presented in this short review, with an emphasis on experimental studies of nanostructures obtained by plasma deposition for fuel cells and on molecular modeling of materials for hybrid organic-inorganic photovoltaics.

Nanoscale phase separations in quantum materials

Augusto Claudio MARCELLI [1,2]

[1] *INFN - Laboratori Nazionali di Frascati, Via E. Fermi 40, 00044 Frascati, Italy*
[2] *RICMASS, Rome International Center for Materials Science Superstripes, Via dei Sabelli 119A, 00185 Rome, Italy*

E-mail: marcelli@lnf.infn.it

Being a fast and local probe of a selected atom X-ray Absorption Spectroscopy represents a powerful technique suitable to investigate heterogeneous systems down to the micrometer scale and below, using small spots. Actually, XANES (X-ray Absorption Near Edge Structures) is an almost unique spectroscopic method when applied to investigate the nature of multi-scale quantum materials, complex systems well beyond the description of disordered systems, and with multi-scale structure and dynamics unavoidably entangled.

Complex lattice architectures can be associated to transition metal and rare earth oxides and to many superconductor materials such as cuprates or pnictides. Actually these systems offer a rich variety of nanoscale structural, electronic and magnetic phases sometime coexisting among them and whose interplay is at the origin of their mesoscopic and macroscopic behaviors.

Probing morphology and phase distribution in complex systems at multiple length scales is then mandatory. Standard experimental probes such as electron microscopy or atomic force microscope, being sensitive to the surface and to a limited numbers of layers below the surface are not able to recognize the presence of different nano-scale phases. Other techniques looking at the k-space such as X-ray diffraction (XRD), neutron diffraction, and angular resolved photoemission, provide only non-local and space averaged information. At variance, local structural probes such as micro-X-ray Absorption Near Edge structure (μ-XANES) may investigate nanoscale structures and nanoparticles being real bulk experimental methods with no time or spatial averaging.

I will present and discuss μ-XANES data of La_2CuO_{4+y}, the simplest cuprate superconductor with mobile oxygen interstitials that exhibits a bulk multiscale structural phase separation. Actually μ-XANES mapping at the La L3-edge provides a strong experimental support to the percolative superconductivity scenario in high temperature cuprates superconductors.

Photoexpansion in a-As_2S_3: a possible new mechanism

Iosif-Daniel SIMANDAN, Florinel Sava, Adam Lőrinczi, Alin Velea, Mihai Popescu

National Institute of Materials Physics, Atomistilor 405A, RO-077125, P.O. Box MG.7, Magurele, Ilfov, Romania

E-mail: simandan@infim.ro

Thin amorphous As_2S_3 films show a giant photoexpansion of ~5 % upon femtosecond laser illumination and this expansion remains after switching off the laser beam [1-4]. To understand the structural modifications which occur during the photoexpansion process we assumed a molecular cluster structure of the amorphous As_2S_3 [5-9]. In the frame of the new mechanism proposed to explain the photoexpansion, we suggest that the focused femtosecond laser beam induces electrical charge redistribution on the sulfur atoms of each cluster, which increases the electrical repulsion between sulfur atoms, and thus induces an expansion of the clusters, by network reconfiguration, without breaking the bonds. An increase of the van der Waals distance between molecular clusters also takes place.

[1] A. Velea, M. Popescu, F. Sava, A. Lőrinczi, I. D. Simandan, G. Socol, I. N. Mihailescu, N. Stefan, F. Jipa, M. Zamfirescu, A. Kiss, V. Braic, Photoexpansion and nano-lenslet formation in amorphous As2S3 thin films by 800 nm femtosecond laser irradiation, Journal of Applied Physics 112, 033105 (2012). http://dx.doi.org/10.1063/1.4745021

[2] K. Tanaka, Photoexpansion in As2S3 glass, Phys. Rev. B 57, 5163-5167 (1998).

[3] S. Ramachandran, J. C. Pepper, David J. Brady, S. G. Bishop, Micro-Optical Lenslets by Photo-Expansion in Chalcogenide Glasses Journal of Lightwave Technology, 15(8), 1371-1377 (1997).

[4] H. Hisakuni and K. Tanaka, Giant photoexpansion in As2S3 glass, Appl. Phys. Lett. 65, 2925-2927 (1994).

[5] T. P. Martin, Arsenic sulfide clusters, Solid State Communications 47(2) (1983) 111-114.

[6] F. Billes, V. Mitsa, I. Fejes, N. Mateleshko, I. Fejsa, Calculation of the vibrational spectra of arsenic sulfide clusters, Journal of Molecular Structure 513(1-3) (1999) 109-115 .

[7] R. Holomb, V. Mitsa, P. Johansson, M. Veres, Boson peak in low-frequency Raman spectra of AsxS100-x glasses: nanocluster contribution, Phys. Status Solidi C 7(3–4) (2010) 885–888 / DOI 10.1002/pssc.200982829

[8] M. Popescu, F. Sava, A. Lőrinczi, A. Anghel, Nano-structural configurations in As2S3 glass, Physics and Chemistry of Glasses-European Journal of Glass Science and Technology Part B, 47(2) 154-157 (2006).

[9] M. Popescu, F. Sava, A. Lőrinczi, A new model for the structure of chalcogenide glasses: The closed cluster model, Journal of Non-Crystalline Solids, 355 (37-42), 1815-1819 (2009).

Transducing mechanism of ammonia detection using $BaSrTiO_3$

C. E. SIMION [1], A. Stănoiu[1], R. M. Piticescu[2]

[1] National Institute of Materials Physics, Atomistilor 405bis, P.O. Box MG-7, 077125, Bucharest-Magurele, Romania
[2] National R&D Institute for Non-ferrous and Rare Metals, 102 Biruintei Blvd, Ilfov, Romania

E-mail: simion@infim.ro

Since ammonia (NH_3) possess sever corrosive behavior, especially in the presence of humidity, the sensitive material must withstand harsh environments without compromise. Perovskite ceramics like $BaSrTiO_3$ (BST) are promising candidates due to their high chemical and thermal stability. Thick film BST material showed high electrical resistance variations towards different levels of relative humidity (10-70%) when operated at room temperature (Fig. 1).

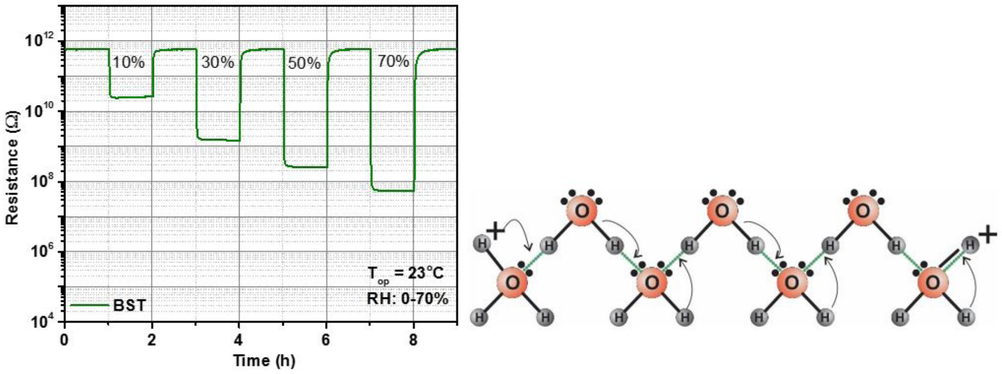


Figure 1. Electrical resistance changes of BST thick film with respect to the RH level @ 23°C and the associated Grotthuss chain reaction

Such behavior was explained based on the capillary water condensation inside the porous structure followed by a Grotthuss like conduction mechanism. The DC readout upon NH_3 exposure indicate a decrease in the electrical resistance with dependent on the target gas concentration. Moreover, an increase in the RH background level induces an improvement in the NH_3 effect (Fig. 2).

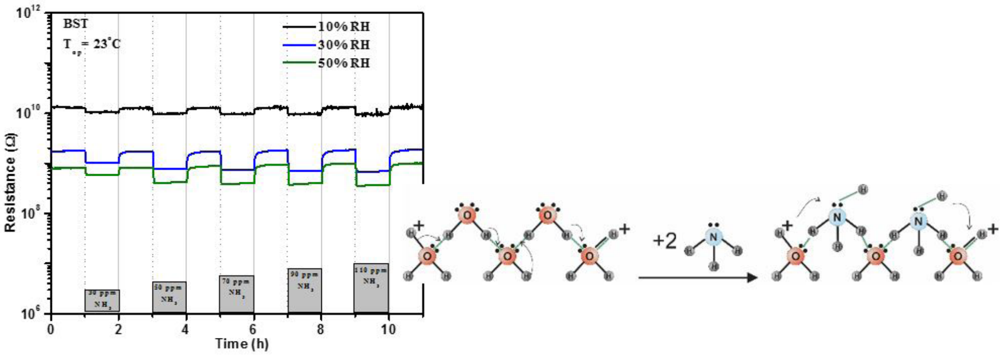


Figure 2. NH_3 exposure effect and the associated transducing mechanism for BST material

These peculiar gas sensing properties are linked to a unique transducing mechanism of NH_3 interaction with the pre-condensed water, different from those encountered in semiconducting metal oxide materials.

The influence of the interlayer type on ferroelectric/dielectric characteristics of multilayered structures

A. BONI, C.Chirila, L. Hrib, R.Negrea, I.Pasuk, C.Ghica, L Filip, I.Pintilie, L.Pintilie

National Institute of Materials Physics Magurele – Bucharest,   P.O. Box MG-7, 077125, Romania

E-mail: andra.boni@infim.ro

Ferroelectric multilayer and superlattices are an important topic of research in the last years due to their unconventional and different properties compared with the constituent layers.

In this study, a thin film of $SrRuO_3$, $CoFe_2O_4$, $BaTiO_3$ or $SrTiO_3$ is used as interlayer in a multilayered structure with two $PbZr_{0.2}Ti_{0.8}O_3$ ferroelectric layers. The studied structures are grown on $SrTiO_3$ (100) substrates by using pulsed laser deposition.

Structural characterization consists in X-ray diffraction (XRD) and transmission electron microscopy (TEM) measurements and reveals an epitaxial relationship between the layers.

The electric/ferroelectric characteristics as ferroelectric hysteresis, dielectric behavior and leakage currents strongly depends on interlayer type. An astounding results is the obtaining of a multiple hysteresis loop associated with an antiferroelectric coupling at interfaces in the cases of $BaTiO_3$ and $SrTiO_3$ interlayers.

CARBON AND NANO

Beyond graphene: hundreds of atomically thin materials

Mircea DRAGOMAN

IMT

E-mail: mircea.dragoman@imt.ro

The talk will be an overview starting form graphene up to the last two-dimensional materials discovered focusing the talk to atomically thin semiconductors and nanomembranes , devices and applications such as tunable electronic and optoelectronic devices devices or artificial synapses for neuromoporphic computation.

Sustainable Carbon Materials and Chemicals from Biomass Hydrothermal Processes

Magdalena TITIRICI

Department of Engineering and Materials Science, Queen Mary University of London
Mile End Road, E14NS, London

E-mail: m.m.titirici@qmul.ac.uk

The creation of new and very importantly greener industries and new sustainable pathways are crucial to create a world in which energy use needs not be limited and where usable energy can be produced and stored wherever it is needed.

New materials based on carbon, ideally produced via inexpensive, low energy consumption methods, using renewable resources as precursors, with flexible morphologies, pore structures and functionalities, are increasingly viewed as ideal candidates to fulfil these goals. The resulting materials should be a feasible solution for the efficient storage of energy and gases.

Hydrothermal carbonization [1] is an ideal technology for the production of such low-cost but highly performing materials out of the most abundant renewable resource on the planet, i.e. lignocellulosic biomass. The practical approach is very simple and consists in placing a biomass precursor inside an autoclave, in water, followed by hydrothermal treatment overnight at 160-200°C. Since the production of carbon materials in general implies harsher and multi-step methodologies along with fossil –based precursors, this process has clear advantages in terms of sustainability and cost.

Here, I wish to present some of our latest results on the production and characterization of nanostructured hydrothermal carbons (HTC) and their use in renewable energy related applications in particular in PEM electrocatalysis and electrode in Na and Li-ion batteries technologies [2], [3].

[1] **M.-M. Titirici**, R. J. White, C. Falco, M. Sevilla, *Energy & Environmental Science* **2012**, 5, 6796-6822.
[2] K. Tang , L. Fu , R J. White , L. Yu , M. Antonietti , J. Maier, **M. M. Titirici** , *Adv. Energy Materials*, **2012**, 2, 873–877.
[3] N. Brun, S. A. Wohlgemuth, P. Osiceanu, **M.-M. Titirici**, *Green Chem.*, **2013**, 15, 2514-2524.

Keywords: *Hydrothermal Carbonization, Porous Carbon, Energy Storage, Heterogeneous Catalysis.*

Anti-Stokes Raman spectroscopy as a method to identify metallic and mixed metallic/semiconducting configurations of multi-walled carbon nanotubes

A. MATEA[1,2], I. Baltog[1], M. Baibarac[1]

[1]*National Institute of Materials Physics, Bucharest, Romania*
[2]*Faculty of Physics, University of Bucharest, Bucharest, Romania*

E-mail: adelina.matea@infim.ro

Surface-enhanced Raman scattering (SERS) studies on different types of carbon nanotubes have gained a special attention in the last decade. We have performed SERS studies in the Stokes and anti-Stokes Raman branches under non resonant (514.5 nm) and resonant (676.4 nm and 647.1 nm) optical excitations on different types of carbon nanotubes: single-walled carbon nanotubes (SWNTs) completely separated in both metallic and semiconductor tubes) [1], double walled carbon nanotubes (DWNTs) [2] and two families of multi-walled carbon nanotubes (MWNTs), one as metallic and semiconductor mixture and another only metallic [3]. The results obtained for SWNTs completely separated in metallic and semiconductor tubes have proven that regardless of the SERS supports used (Au or Ag), the metallic nanotubes do not present an anomalous anti-Stokes Raman emission. Regardless of whether resonant or non-resonant optical excitation is used, only the semiconducting nanotubes produce an abnormal anti-Stokes Raman emission that increases with the excitation light intensity. Based on these results, the interest was also focused on DWNTs for which the radial breathing mode (RBM) made possible the identification of the metallic or semiconducting type of the outer/inner tube in the their architecture. This method regards the difference between the intensities of recorded anti-Stokes Raman spectrum and the anti-Stokes spectrum calculated by applying the Boltzmann relation to the recorded Stokes spectrum. The results indicate that there are RBM lines of the same intensity in both spectra, as well as RBM lines of higher intensity that are observed in the calculated spectrum. When the intensities of RBM lines coincide in both ranges it is about the metallic tubes and when the intensities of RBM lines are different, they indicate the semiconducting tubes. Next studies have concerned applying the above theory to two families of MWNTs which alternate semiconducting and metallic tubes or only metallic tubes obtained by CCVD method. The former family of MWNTs reveal similar spectra in the Stokes and anti-Stokes branch, denoting an increasing Raman intensity when the glass substrate is replaced with Au or Ag substrate, which indicates the occurrence of the SERS mechanism. The invariance of the Raman intensity in the anti-Stokes branch as a result of the change of the substrate is characteristic of metallic MWNTs fact explained by a Raman light scattering process occurring only within the skin depth of the metallic structure.

References:
[1] M. Baibarac, I. Baltog, L.Mihut, S. Lefrant; J. Raman Spectroscopy, 45, 323, (2014)
[2] M.Baibarac, I. Baltog, A. Matea, L. Mihut, S. Lefrant; J. Raman Spectroscopy, 46, 32, (2015)
[3] M. Baibarac, A. Matea, M. Ilie, I.Baltog, A. Magrez; Analytical Methods, 7, 6225, (2015)

Morphology-driven charge storage properties of trilayer structures with Ge nanocrystals in HfO2

A.M. LEPADATU [a], A. Slav [a], C. Palade [a, b], A.V. Maraloiu [a] , C. Logofatu [a],
S. Lazanu [a], V.S. Teodorescu [a], M.L. Ciurea [a]

[a] *National Institute of Materials Physics, 405A Atomistilor Street, 077125 Magurele, Romania*
[b] *University of Bucharest, Faculty of Physics, 405 Atomistilor Street, 077125 Magurele, Romania*

E-mail: lepadatu@infim.ro

Ge nanocrystals (NCs) embedded in oxides have attracted increasing interest for applications in non-volatile memory (NVM) devices [1,2]. By using NCs of Ge, the charge storage is more efficient and the charge retention is improved. At the same time, HfO_2 as oxide matrix represents the best choice due to its high dielectric permittivity and asymmetric band offsets enabling the decrease of device area and of leakage currents [3]. However, the challenge for these devices represents the controlling of NC parameters related to density and spatial positioning (distance from the substrate and lateral inter-NCs separation distance) that determine the charge storage properties. Moreover, understanding the relationship between morphology and charge storage properties is necessary.

Our approach is to prepare trilayers with intermediate layer of Ge NCs with high density and good vertical and lateral separation, acting as storage nodes. For this, we deposit by magnetron sputtering trilayers of HfO_2/Ge /HfO_2 on Si substrates, with tunnel and control HfO_2 layers and intermediate Ge layer. Then, we conduct the Ge NCs formation process using rapid thermal annealing under controlled conditions, i.e. temperature, attention being paid to limiting the Ge diffusion effect. In this work, we discuss samples annealed at 600 and 850 °C. The trilayers morphology investigations directed on Ge NCs formation, their size, density and position were carried out using HRTEM, HAADF-STEM, Raman and XPS characterization techniques. The charge storage properties are studied by capacitance-voltage (C – V) investigations in the 100 kHz – 1MHz frequency range.

The morphology investigations demonstrate the formation of high density Ge NCs (5 – 7 nm) in the intermediate layer of structures annealed at 600 °C, being located at precise (as-deposited) position and having good inter-NCs separation distances. The C – V curves measured on these trilayers show hysteresis loops with highest memory window of ~1.3 V [4]. In contrast, the annealing of trilayers at 850 °C produces Ge NCs with smaller density as the enhanced Ge diffusion effect produces the spreading of Ge atoms into HfO_2, and consequently the hysteresis loops have smaller memory windows. Both kinds of trilayers show frequency-independent memory windows due only to charge storing inside Ge NCs. These results reveal the strong correlation between morphology and charge storage properties of trilayers based on Ge NCs in HfO_2.

[1] R Bar, R Aluguri, S Manna, A Ghosh, PV Satyam, SK Ray, Appl. Phys. Lett. 107, 093102 (2015)
[2] D Vasilache, A Cismaru, M Dragoman, I Stavarache, C Palade, AM Lepadatu, ML Ciurea, Phys. Status Solidi (a) 213, pp. 255–259 (2016)
[3] VA Gritsenko, TV Perevalov, DR Islamov, Phys. Rep. 613, pp. 1–20 (2016)
[4] A Slav, C Palade, AM Lepadatu, ML Ciurea, VS Teodorescu, S Lazanu, AV Maraloiu, C Logofatu, M Braic, A Kiss, Scripta Mater. 113, pp. 135–138 (2016)

Functional metal oxide thin films from electric field assisted aerosol assisted chemical vapour deposition

Russell BINIONS [1,2]

[1] *School of Engineering and Materials Science, Queen Mary University of London, Mile End Road, London E1 4NS, United Kingdom*
[2] *Materials Research Institute, Queen Mary University of London, Mile End Road, London E1 4NS, United Kingdom*

E-mail: r.binions@qmul.ac.uk

Titanium, vanadium or tungsten oxide thin films were deposited via aerosol assisted chemical vapour deposition on to fluorine doped tin oxide coated glass or gas sensor substrates. A potential difference was applied between the top plate and substrate or across the sensor substrate electrodes during the deposition to generate an electric field. The films produced were analysed and characterised by X-ray diffraction, scanning electron microscopy, X-ray photoelectron spectroscopy, Raman spectroscopy, contact angle as well as functional tests such as variable temperature UV/Visible spectroscopy, photocatalytic activity or gas sensitivity. It was found that the presence of an electric field during deposition could lead to a marked change in the microstructure and therefore the functional properties of the deposited films; specifically improved wetting, gas sensitivity, photocatalytic and thermochromic properties. An increase in field strength could lead to a reduction in crystallite and agglomerate size, new and unusual crystallographic orientations when compared to films grown without the presence of an electric field.