





- 14,00 - 14,30** V. Atanassova, P. Zahariev “Work visit to the Polish Academy of Sciences”
- 14,30 - 15,00** J. A. Weicht, F. U. Hamelmann “Simulation of thin film silicon-based solar modules”
- 15,00 - 15,30** **Coffee break**
- 15,30 - 16,00** E. Radeva, D. Mitev, L. Peeva “Polymeric membranes modified by plasma polymerization”
- 16,00 - 16,30** S. Varbey “Work visit to FH Bielefeld, Germany”
- 16,30 - 17,00** A. Donkov “Report on Work Visits to the Fachhochschule Bielefeld, Germany and the International Laboratory on High Magnetic Fields and Low Temperatures Wroclaw, Poland”

### Wednesday, 14.09.2016

- 9,30 - 12,30** **Social Event (visit a museum in Sofia)**
- 12,30 - 14,00** **Lunch**
- 14,00 - 14,30** M. Czopnik, N. Ivanov “Alternating  $S=1$ ,  $s=1/2$  chain as an example for spinnematic systems”
- 14,30 - 15,00** I. Ilievska, A. Stoyanova-Ivanova, A. Zaleski “Analysis of elemental composition, structure characterization and magnetic measurements of materials used in orthodontic medicine”
- 15,00 - 15,30** **Coffee break**
- 15,30 - 16,00** S. I. Boyadjiev, K. A. Gesheva “ALD and CVD deposited transition metal oxides thin films for electrochromic applications”
- 16,00 - 16,30** K. A. Gesheva “Chromogenic smart metal oxides films and how INERA project helped building up international research team for their characterization”
- 16,30 - 17,00** E. Dimova “General report: Work Package 3, INERA project”
- 17,30 - 20,00** **Working dinner**



## ULTRACOLD ION BEAMS USING LASER COOLING

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Focused ion beam instruments are indispensable tools for the semiconductor industry due to their ability to image and modify structures on the nanometer length scale. For milling and deposition, the industry standard is the gallium liquid-metal ion source which enables a resolution of 5-10 nm at a current of a few pA. With the quest towards smaller features on integrated circuits, there is a need for novel ion sources that allow for better resolution. Several research groups are working towards applying laser-intensified alkali-metal ion beams for this purpose [1]. Such ultra-low temperature (1 mK) ion beams can be created by laser cooling and photo-ionization of a thermal atomic beam or vapor. The Rb ion source under development in Eindhoven in collaboration with FEI Company starts with a high-flux Knudsen cell connected to a collimating tube. The brightness of the atomic beam is greatly increased by laser cooling and compression in the transverse direction using a compact magneto-optical device. Calculations show that, for rubidium-85, an equivalent atomic beam brightness of  $10^7$  A/m<sup>2</sup> sr eV can be achieved in this way [2]. The resulting cold beam of atoms is converted to an ion beam by near-threshold photo-ionization inside an optical build-up cavity surrounding an accelerator structure. Subsequent disorder-induced heating can have disastrous effects on the beam's brightness. Particle tracking simulations reveal a strategy to suppress the heating by creating a so-called pencil beam. Analytical calculations [3] that include the finite brightness of the beam as well as chromatic and spherical aberrations of a realistic focusing column nevertheless show that a focal spot of  $\approx 1$  nm at a current of 1 pA or 5 nm at currents up to 20 pA is possible.

[1] For an overview see: Kevin Weatherill and Edgar Vredendregt, *Physics World* **25** 28 (2012) and J. J. McClelland et al, arXiv:1510.08673 (2015)

[2] S.H.W. Wouters et al., *Phys. Rev. A* **90** 063817 (2014)

[3] G. ten Haaf et al., *J. Appl. Phys.* **116** 244301 (2014)



## **JOINT RESEARCH ON NANOSTRUCTURED THIN METAL OXIDES AND NITRIDE FILMS AND THEIR POSSIBLE APPLICATIONS**

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I will report the results of my secondments that have been realized during the years of the Project INERA. The aims of my visits to INERA Project partner organization and namely, to professor Ion N. Mihailescu, head of the Laboratory “Laser – Surface Plasma Interaction“ of the National Institute for Lasers, Plasma and Radiation Physics (NILPRP), Romania, were strengthening the collaboration between ISSP Bulgaria and NILPRP and extending the collaboration by involving the Institute of Physical Chemistry (IPC), Romania.

My secondments have achieved their objectives, as the contacts with partners were thorough, new knowledge was received and cooperation between ISSP-BAS NILPRF and IPC was established. Joint research on nanostructured thin metal oxides and nitride films has been conducted and the possible applications of these multifunctional films have been considered. The results have been prepared for presentation at different scientific events and for publication in relevant scientific journals.



## QUANTUM CONTROL VIA COMPOSITE PULSES

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I examine the method of composite pulses and its application for quantum control. The technique of composite pulses uses a sequence of pulses with relative phases, used as control parameters. I show how composite pulses can be used to improve different adiabatic techniques (RAP and STIRAP). Then I show how one can construct simple quantum gates, using composite pulses. As an example I examine the two-state quantum phase gate. Finally, I present a method to construct ultra-broadband and ultra-narrowband composite pulses, which produce better excitation profiles at the expense of a finite error tolerance.





## **IMPEDANCE SPECTROSCOPY AND DIELECTRIC RELAXATION INVESTIGATIONS IN NANOSTRUCTURED SOFT MATTER SYSTEMS**

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The soft matter nanostructured materials like liquid crystal systems, gels, polymeric materials, electrochromic materials, solid electrolytes, super capacitors, etc. exhibit a remarkably rich phase behavior leading to a wide range of viscoelastic and other interesting properties. This rich variety can be explained by the mesoscopic size of the components which the materials consist of. They are larger than molecules, but smaller than macroscopic. These components can be nanoparticles, chains, droplets and other. As their interactions can be extremely diverse, the resulting properties of soft materials have become a highly fascinating field of study. The development and understanding of those high-tech materials requires a detailed knowledge of the complex dielectric and conductivity function response.

In this presentation, we will report the details of electrochemical impedance spectroscopy (EIS) measurements and dielectric studies. It will demonstrate the extraordinary potential of EIS and their applications. Impedance spectroscopy offers an accurate determination of the interfacial and diffusion processes, since they are separated on the frequency scale. The EIS data are usually fitted to a Randles circuit, which consists of an Ohmic resistance, a charge transfer resistance, a double layer capacitance, and a Warburg impedance.

We are going to discuss the way of measurements, dielectric properties and used equipment (measuring cells, impedance analyzers) and different models of relaxations (Debye, Havriliak-Negami models).

Also in the briefing we will present our efforts with the technique for EIS and dielectric measurements available for the material characterization of nanostructured soft materials at ISSP-BAS. We will give our overview on the EIS experimental technique, as well as will elaborate on the analysis of dielectric and impedance spectra. Modification of EIS, AC voltammetry of metal-oxide films will be discussed as well.



## PERIODICAL SURFACE NANOSTRUCTURES INDUCED BY FEMTOSECOND LASER

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Laser Induced Periodical Surface Structures – LIPSS, commonly known as ripples, obtained in metals under femtosecond laser irradiation have been extensively investigated by many research groups. Depending on the irradiation conditions, such as laser fluence, number of laser pulses or laser wavelength, different morphology and ripple periods have been obtained: Low Spatial Frequency LIPSS (LSFL) with a periodicity close to the incident laser wavelength,  $\lambda$ , with orientation perpendicular to the laser polarization, and High Spatial Frequency LIPSS (HSFL) with a periodicity from  $\lambda/2$  up to  $\lambda/10$ , with orientation parallel to the laser polarization. Such micro- and nano-textured surfaces have important applications such as fabrication of biomimetic substrates for cells growth and proliferation, surfaces with modified tribologic or wetting properties, security marking.

In our previous experiments, nanostructured surfaces were obtained on extended areas of samples of various materials by irradiation with femtosecond laser pulses in air. Different samples such as Cr, Ni, Ti, W, Si, ZnO were processed by linearly polarised Ti:Sapphire laser, at repetition rate of 2 kHz, pulse duration of 200 fs, and at two different wavelengths, the fundamental near-IR radiation at 775 nm, and the SHG at 387 nm. A laser scanning head with galvanomirrors and focusing lens with 100 mm focal length was used for fast processing of the samples. The irradiation conditions such as laser fluence and scanning speed were varied for each metallic sample. The nanostructures were investigated by SEM, AFM. Different morphology and ripple periods have been obtained depending on the radiation wavelength and the irradiation conditions (environment, scanning speed, laser fluence, etc).

Our previous experimental observations are complemented by calculations based on the classical interference theory, surface plasmon and SHG theories. However, the SHG mathematical model doesn't provide reliable predictions and requires further investigations. In order to achieve this, using a large interval of wavelengths for the incident radiation provides a significant advantage. Experimental results and the formation mechanisms of ripple structures are discussed.





## ATOMIC LAYER DEPOSITION AND CHARACTERIZATION OF THIN FILMS

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By the Project INERA in ISSP-BAS was build clean room and there were installed two states of art deposition tools: PECVD and PEALD. PECVD on Oxford Instruments is designed to grown carbon nanotubes and graphene. PEALD on BENEQ (TFS – 200) is for oxide nanofilms and coverings.

In this presentation will be shown an overview of the atomic layer deposited (ALD) films and structures grown and investigated during the Project INERA. ALD films and structures were obtained at ISSP-BAS and at the INERA partner – IP-PAS. Some of the characterizations were performed at the INERA partners.

At the PEALD system BENEQ TFS-200 at ISSP-BAS are available 4 liquid: H<sub>2</sub>O; TMA, DEZ, BTBAS; and 3 solid precursors: Ferrocene; Cobaltocene; and Nickelocene. The obtained films after optimization of thermal grown process were: ZnO, Al<sub>2</sub>O<sub>3</sub>, ZnO:Al<sub>2</sub>O<sub>3</sub>, Co-O, Ni-O, Fe-O and AlN. As oxidant were used H<sub>2</sub>O for ZnO and Al<sub>2</sub>O<sub>3</sub> or Ozone for metalocenes. The structure and properties of the films are strongly depending on the substrate therefore we used different substrates: Si, glass, quartz and PAA.

At the IP-PAS three different types of structures were obtained: in the first one, ZnO films were deposited on Al<sub>2</sub>O<sub>3</sub> buffer layers; in the second one, ZnO films were deposited directly on Si substrate with TiO<sub>2</sub> films placed on the top; and in the third one, ZnO films were sandwiched between a bottom Al<sub>2</sub>O<sub>3</sub> and a top TiO<sub>2</sub> films. Moreover there were grown different high-k dielectric nanolaminates HfO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>.

Some of the deposited films were well characterized with AFM, SEM, XRD, XPS, Ellipsometry, Optical measurements, Resistance measurements, Impedance Spectroscopy.

Because of the high film density, low pin hole levels, perfect 3D conformality, ultra high aspect ratio (>2,000:1), large area thickness uniformity, atomically flat and smooth coating, ALD films could be used in various applications beyond competition. Some of the ALD films applications are: nanomaterials, nanodevices, displays, memories, nanocoatings, gas/bio sensors, solar and fuel cells, nanomedicine, pharmacy and cosmetics.





## FLUID MODELING OF COMBINED PLASMA SOURCE LASER ABLATION- HOLLOW CATHODE GLOW DISCHARGE

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The laser ablation-hollow cathode discharge system couples the laser ablation capability for microprobe sampling (thin film deposition, nanoparticles creation, and material introduction) with hollow cathode glow discharge plasma (surface plasma modification, emission, and absorption spectroscopy). The combined technique is advantageous to:

- the hollow cathode glow discharge by the extended number of materials (nonconductive) which can be introduced, analyzed and modified in the discharge plasma;
- the laser-induced plasma due to the additional excitation/ionization and modification of the ablated material in the discharge.

The promising experimental results obtained with the coupled sources [1, 2] are accompanied with little or no theoretical work done on this system. As plasma modeling is capable of interpreting the observed experimental results and giving a better understanding of the underlying plasma processes, it is of interest to investigate this combined source from a theoretical point of view.

We report on a drift-diffusion model of a combined laser ablation-hollow cathode discharge plasma emission source. The model is created as a part of the PLASIMO [3] toolkit, designed in the group Elementary Processes in Gas Discharges, Eindhoven Technical University, Eindhoven, The Netherlands. It uses its drift-diffusion module [4]. The model is applied for simulation a beam of ablated species injected into the glow discharge plasma. The model follows the time evolution of the interaction dynamics and outputs the spatial distributions of particle densities, electron energy and discharge voltage. The model allows setting the starting moment and the duration of the ablated atomic beam injection. The module enables the investigation of several injection cycles, which is used for simulation of laser ablation introduction with multiple pulses.

The model results show that during the ablated atoms introduction cycle, there is an enhancement of the densities of the main discharge species and pronounced change in their spatial distributions. Analysis of particle creation and destruction reactions is performed. The analysis shows that the creation of a large population of target ions near the injection site is mainly due to direct electron and stepwise ionization processes. It is observed that in the same area, enhancement of the ion cathode sputtering takes place. After the end of the introduction cycle, the hollow cathode plasma returns quickly to steady-state operation.

References:

1. T. Naeem, H. Matsuta, K. Wagatsuma, *The J. Soc. for Anal. Chem.*, 20 (2004)
2. C. González de Vega, C. Álvarez Llamas, N. Bordel, R. Pereiro, A. Sanz-Medel, *Anal. Chim. Acta* 877 (2015)
3. J. van Dijk, K. Peerenboom, M. Jimenez, D. Mihailova and J. van der Mullen. *J. Phys. D: Appl. Phys.*, 42 (2009)
4. D. Mihailova, J. van Dijk, M. Grozeva, G. Hagelaar and J. van der Mullen. *J. Phys. D: Appl. Phys.* 43 (2010)



## ELECTRICAL CHARACTERISTICS OF MULTILAYERED $\text{HfO}_2 - \text{Al}_2\text{O}_3$ CHARGE TRAPPING STACKS DEPOSITED BY ALD

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The electrical characteristics of Metal–high- $k$  ( $\text{HfO}_2\text{--Al}_2\text{O}_3$ )–Silicon (MOS) structures have been investigated in order to assess their applicability in non–volatile charge trapping memory devices. The stacked  $\text{HfO}_2 - \text{Al}_2\text{O}_3$  high- $k$  charge trapping layers have been fabricated on Si substrates by Atomic Layer Deposition (ALD). Two types of charge trapping layers with different number of  $\text{Al}_2\text{O}_3$  deposition cycles were prepared. To evaluate the effect of post deposition annealing (PDA) on the electrical and charge storage properties of the films part of the samples was subjected to annealing in dry  $\text{O}_2$  at  $600^\circ\text{C}$ . MOS capacitors were patterned by photolithography employing Al as gate and backside electrode. The electrical properties of the capacitors were evaluated by capacitance–voltage (C–V) and current–voltage (I–V) measurements.

The obtained results revealed that the dielectric properties of multilayered  $\text{Al}_2\text{O}_3 - \text{HfO}_2$  stacks can be effectively modified by the thickness of  $\text{Al}_2\text{O}_3$  sublayers. The alumina content affects mainly the effective dielectric constant, the initial oxide charge and its response to the thermal treatments, while the impact on the leakage currents is weak. The conduction mechanisms of the stacks is not affected by the  $\text{Al}_2\text{O}_3$  content and the current is governed by hopping conduction and Poole-Frenkel mechanism. The post deposition annealing densifies the stacks and increases the density of the existing defect states in case of stacks with thinner  $\text{Al}_2\text{O}_3$  and introduces new type of defects in structures with higher  $\text{Al}_2\text{O}_3$  content manifested via the change of the oxide charge sign. The higher trap density of stacks with smaller  $\text{Al}_2\text{O}_3$  content ensures wider memory window, which is further widened by oxygen annealing. Different type of defects participate in the charge trapping and in the conduction in these stacks, since the leakage is improved after annealing. Annealed stacks with smaller  $\text{Al}_2\text{O}_3$  content also exhibit outstanding retention and endurance characteristics. The results clearly indicate existence of an optimal alumina content providing maximum performance



## IMPLEMENTATION AND USE OF ALGORITHM FOR CHEMICAL PATHWAY ANALYSIS IN PLASIMO

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In plasma research the mixtures under investigation have become increasingly complex with regards to chemical composition. These rich compositions contain large numbers of chemical species and huge amounts of chemical reactions. The sheer size of these chemistries pose a problem when it comes to numerical efforts to study these plasmas. No longer is analysis by hand a viable option, and one has to resort to automated algorithms. In this project one such algorithm, introduced by Lehmann [1], has been implemented in the plasma modeling platform PLASIMO [2].

The analysis of complex chemical systems requires the determination of pathways, i.e., reaction sequences, that produce or destroy chemical species of interest. Furthermore, it is necessary to determine the most significant pathways producing or consuming the chemical species. The algorithm takes as input a set of chemical reactions and their rates, and species densities, both of which result from a previous calculation. Based on this data the algorithm chooses so-called “branching points” based on the lifetimes of species. By connecting pathways at these short lived species they can be eliminated from the chemistry. Additionally, pathways that turn out to have insignificant contribution can be discarded, though their contribution is taken into account.

The algorithm has been implemented as part of PLASIMO's Global Model module [3] using the programming language C++. It has been applied to various test chemistries, such as argon and nitrogen plasmas.

### References:

- [1] R. Lehmann, “An algorithm for the determination of all significant pathways in chemical reaction systems”, *Journal of atmospheric chemistry* 47: 45–78, (2004)
- [2] <http://plasimo.phys.tue.nl>
- [3] W. Graef, “Zero-dimensional models for plasma chemistry”, PhD thesis, Eindhoven University of Technology, (2012)



## POLYETHYLENE OXIDE BASED NANO COMPOSITE SOLID POLYMER ELECTROLYTES FOR SODIUM ION BATTERY APPLICATIONS

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Solid-state polymer electrolytes (SPEs) have attracted great attention by the researchers in the field of rechargeable metal-ion battery applications, to overcome a great deal of drawbacks of conventional liquid electrolytes. SPEs are flexible and can conform to any battery shape; they eliminate the need for a separator and can significantly improve the safety and stability of batteries due to their non-leakage and nonreactive characteristics. In complementing to Li-ion battery technology, sodium (Na) based rechargeable batteries (SIBs) have recently captured much attention owing to their characteristic properties such as environmentally friendly, non-toxic, low cost and earth abundant materials. Significantly, reinforcement of nanometer sized materials (such as TiO<sub>2</sub> and Graphene Oxide sheets) with SPE systems can tune microstructural, thermal properties and electrochemical performances of SPEs. Polyethylene oxide (PEO) is one of the widely investigated host polymer for synthesizing solid polymer electrolytes (SPEs) for alkali metal ion-conducting batteries due to its high electrochemical stability, good solvation power, complexation and ion dissociation abilities.

Free-standing and NaIO<sub>4</sub> salt complexed 'PEO/PVP' solid polymer electrolytes have been fabricated by using a solution casting technique. The modification in crystallinity of solid polymer electrolyte and the interactions of Na-ions with the host of blend electrolytes are characterized by X-ray diffraction (XRD), Micro Raman and Fourier transformed infra-red (FTIR) spectra, which reveal the degree of Na-ion solvation by PEO oxygen atoms (EO:Na). The surface morphological features and thermal properties of blend electrolytes are investigated by Scanning electron microscopy (SEM) and Thermogravimetric analysis (TGA). The ionic conductivities of the films are investigated by impedance analysis from 1 MHz to 0.1 Hz within the temperature range 303 K – 343 K. 'PEO/PVP/NaIO<sub>4</sub> (10 wt%)' blend electrolyte demonstrated room temperature conductivity of  $1.57 \times 10^{-7}$  S/cm. Series of polymer blend electrolytes consisting different concentrations of graphene oxide (GO) and TiO<sub>2</sub> nano particles are prepared using solution cast method. Transmission electron microscopy (TEM) is employed to understand the distribution of doped nano sized materials in host blend electrolytes. Graphene oxide doped 'PEO/PVP/NaIO<sub>4</sub> (wt% of 10)' electrolyte demonstrated room temperature conductivity in the order  $10^{-4}$  S/cm. Dielectric and electric modulus parameters of blend electrolytes are analysed as a function of graphene oxide. Conductivity and dielectric studies of TiO<sub>2</sub> nano particles doped blend electrolytes are in progress.





## FEMTOSECOND LASER SYSTEM

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The laser department at ISSP obtained, within INERA project, a unique laser system for Bulgaria. The new femtosecond laser system allows significant expansion of the research field and provides investigations in the most advanced areas of photonics. The purchased femtosecond laser system (Spectra-Physics) includes Ti-sapphire oscillator (Mai Tai SP); Ti-sapphire regenerative amplifier (Spitfire Ace 35F1K), with pulse duration of  $<35$  fs and pulse energy  $> 6$  mJ; diode pumped Nd: YLF laser (Empower-45); an optical parametric amplifier (TOPAS-Prime), with wavelength of output radiation from 240 to 2600 nm. An important task has been to conduct review and analysis of promising new areas of femtosecond laser application. As well as promoting the potential of the system to the College at the institute and the potential external users. Last and not at least, to identify new applications in various interdisciplinary areas. Knowledge and experience has been exchanged with the project partners in the field of laser physics with ultra-fast lasers.

The research with the femtosecond laser up to now are grouped into several areas:

1. Laser materials processing, processing of thin films, micro and nano machining, modification and nanostructuring of surfaces.
2. Quantum and nonlinear optics – it is under preparation an experiment to study the nonlinear polarization properties of high-energy femtosecond radiation propagation in atmosphere.
3. Plasma Physics - experimental and theoretical studies of plasma cloud formed by femtosecond laser irradiation applied for different materials in vacuum and under atmospheric pressures; pulsed laser deposition of thin films and nanostructures.
4. Laser Induced Spectroscopy (LIBS) with femtosecond pulses, applications.



## **WORK VISIT TO THE POLISH ACADEMY OF SCIENCES**

**MAY 9<sup>TH</sup> – JUNE 12<sup>TH</sup> 2016**

Victoria Atanassova, Peter Zahariev

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We visited several laboratories at the Polish Academy of Sciences as *Molecular photophysics, Laser spectroscopy, Physics of strongly correlated materials, Structure and molecular interactions, High-pressure spectroscopy* and the *Center of plasma and laser engineering*. Our aim was to get acquainted with their equipment, research activity and new experimental techniques and to discuss future research collaborations. During our work visit we did some experiments on laser micromachining, spectroscopy and other applications.



## SIMULATION OF THIN FILM SILICON-BASED SOLAR MODULES

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Silicon-based thin film tandem solar cells consist of one amorphous (a-Si) and one microcrystalline ( $\mu\text{c-Si}$ ) silicon solar cell. The Staebler - Wronski effect describes the light-induced degradation and temperature-dependent healing of defects of silicon-based solar thin film cells. The solar cell degradation depends strongly on operation temperature. Until now, only the light-induced degradation (LID) of the amorphous layer was examined in a-Si/ $\mu\text{c-Si}$  solar cells. In our presented work we show the changing of the parameters of each diode model during the light-induced degradation at different degradation temperatures (30°C, 50°C and 70°C). Furthermore we present the extracting the parameters for the diode model of solar cells for measured voltage-current-curves and how to simulated this for different climatic regions to prevent current mismatching: During the metastability of thin film silicon.-based solar modules the different parameters are changing: Meanwhile the serial-resistance increases by decreasing degradation temperature, the parallel resistance show no significant changing. Also the saturation current of the diode decreases, which illustrate a decreasing amount of dangling bonds in the energy gap. By this decreasing amount, the efficiency increases as described by the Staebler-Wronski effect.

Distinguishing between conditions without direct irradiation (clouded sky) and partial direct irradiation (clear sky) is obligatory for the simulation of different silicon-based solar modules: Solar modules of a-Si show no significant difference between clouded sky and clear sky conditions, while the performance ratio (ratio between the actual efficiency and the efficiency of the data sheet) of a-Si/ $\mu\text{c-Si}$  solar modules at clear sky is lower than the performance ratio of clouded sky. The performance ratio of c-Si solar modules at clear sky conditions is even lower than the performance ratio at clouded sky conditions.



## POLYMERIC MEMBRANES MODIFIED BY PLASMA POLYMERIZATION

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During the working visit to Imperial College, London, a number of experiments and investigations planned in conjunction with the host country "Department of Chemical Engineering" headed by Prof. Andrew Livingston and with the active participation of Dr. Ludmila Peeva from the same department had made.

The research was mainly on samples of membranes modified by deposition of thin polymer films which were synthesized in plasma reactor, available at the Acoustoelectronics laboratory (precursors pentane perfluorohexane, hexamethyldisiloxane), as well as in the new PECVD system "Oxford Nanofab Plasmalab System 100" (precursors methane-argon and acetylene-argon). With these precursors were modified total of 66 different model hydrophobic nanomembranes types of PEEK and PBI, and ultramembranes PAN, Ulten 1000 PVDF.

During the visit real tests of the experimental modified membranes were carried out, their porosity is estimated both before and after the plasma modifications. Studies on the permeability and selectivity of the modified membranes were carried out on 8-position cross-flow-filtration system with markers polystyrene with various molecular weights.

SEM-microscopy of the above mentioned objects – modified membranes and samples with polymers on silicon and glass, prepared together with membranes - in combination with the ATR-FTIR spectra of the treated membranes and the polymers were collected in order to characterise them.

The results will help in the further improvement of the models on membrane processes ranging from small laboratory units, through midrange (MaxiMem) to the large industrial systems.

The discussion on the obtained CVD modified membrane properties and its applications as well as seeking opportunities for future collaboration and exchange of mutually beneficial information were carried out.







**WORK VISIT TO FH BIELEFELD, GERMANY**  
**JUNE 1<sup>TH</sup> – AUGUST 15<sup>TH</sup> 2016**

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I visited the group of Prof. Christian Schroeder from the Department of Engineering Sciences and Mathematics of the Fachhochschulen Bielefeld - University of Applied Sciences. The aim was to exchange scientific ideas and gain an experience in the broad field of Theoretical Physics with a special emphasize to the narrow field of Nanostructured Magnetic Materials. During my work visit I was acquainted with theoretical approaches in the field of Theoretical Physics like investigation of the dynamical behaviour of finite rings of classical spin vectors interacting via nearest - neighbors isotropic exchange in an external magnetic field.



**REPORT ON WORK VISITS TO THE FACHHOCHSCHULE BIELEFELD  
BIELEFELD, GERMANY, 13.06 – 26.06.2016  
AND  
THE INTERNATIONAL LABORATORY ON HIGH MAGNETIC FIELDS AND LOW  
TEMPERATURES WROCLAW, POLAND, 20.07 – 24.07.2016**

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During my two short work visits, at the FH Bielefeld, and at the formerly International Laboratory on High Magnetic Fields and Low Temperature in Wroclaw, I participated in the exchange of knowledge with members of the group of Prof. C. Schroeder (FH Bielefeld) and had useful conversations with the staff members of the International Laboratory, prof. D. Gajda, among others. Particularly useful was also the opportunity to make contacts with members of the nearby institutions, at the Department of Physics at the University of Bielefeld, prof. J. Schnack, and at the Institute of Low Temperature and Structural Research (INTiBS) of the Polish Academy of Sciences, prof. T. Zaleski and prof. A. Zaleski. During the visit to Bielefeld, part of the work submitted to the proceedings of the InERA conference in Velingrad – 2016 was completed. Both visits were made within a group of members of the Theory Division of the ISSP.



## ALTERNATING $S=1$ , $\sigma=1/2$ CHAIN AS AN EXAMPLE FOR SPINNEMATIC SYSTEMS.

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The impact of frustrating three-site exchange interactions on Heisenberg spin systems is scarcely explored. Based on numerical density matrix renormalization group and exact diagonalization calculations, in this work we explore the quantum phase diagram of the Heisenberg chain constructed from alternating  $S = 1$  and  $\sigma = 1/2$  site spins and containing extra isotropic exchange interactions. We demonstrate that the three-site terms can stabilize some specific partially-polarized spin states as well as a doubly generate non-magnetic gapped state.



## ANALYSIS OF ELEMENTAL COMPOSITION, STRUCTURE CHARACTERIZATION AND MAGNETIC MEASUREMENTS OF MATERIALS USED IN ORTHODONTIC MEDICINE

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The investigations at Institute of Low Temperature and Structure Research - PAS were focused on the topic “Analysis of elemental composition, structure characterization and magnetic measurements of NbTi, NiTi and CuNiTi archwires used in orthodontic medicine”.

The tasks of the studies were as follows:

- Analysis of the morphology and composition made on Scanning Electron Microscope (SEM).
- Structural analysis made by X-ray Powder Diffraction (XRD) technique.
- Thermodynamic analysis made by Differential Scanning Calorimetry (DSC).
- Among the additional tasks realized during my stay were: - magnetic measurements on PPMS (Physical Properties Measurements System) for the superconducting NbTi alloy and resistivity investigation of some chosen samples.

The use of the methods such as SEM, DSC and XRD for investigation of materials was a key point of the performed work that did not only deal with theoretical aspects, but also had a strong experimental contribution.

The results obtained by XRD will show if the structure of orthodontic archwires as obtained and after different usage time in the mouth, during treatment were proving the degradation of the wire and possible reason of such changes. From SEM it can be noticed that the changes are both on the surface of the used archwires and in its volume.

DSC method has potential ability to detect shifts in transformation temperatures of finished orthodontic archwires that are strained at different levels. This may serve as a marker of the changes and applicability period of the wires used by patients.

Also from magnetic measurements made on PPMS of the investigated archwires as-received and used archwires may be used for above purpose. Until now there is no information for such investigation for those materials.

The results obtained from all methods will provide us information about the time in which the archwires retains its properties.

The study of orthodontic archwires (NbTi, NiTi and CuNiTi) offered on the Bulgarian market, used during the treatment will be useful for the healthcare system and will provide information for comparison with similar results obtained from other producers.



## ALD and CVD DEPOSITED TRANSITION METAL OXIDES THIN FILMS FOR ELECTROCHROMIC APPLICATIONS

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Many transition metal oxides are widely used for electrochromic applications. Among them  $\text{WO}_3$ ,  $\text{MoO}_3$  and  $\text{V}_2\text{O}_5$  show high performance in a number of industrial applications, such as “smart windows”, large-scale displays, switchable optical coatings and many others. Their properties might be further improved by making composites of them with other semiconductor oxides. In the present research, by using chemical vapour deposition (CVD) and atomic layer deposition (ALD) we prepared various thin films of these oxides and combinations of them, and characterized them for electrochromic applications.

The composition, structure and morphology of the pure and composite films were characterized by scanning electron microscopy (SEM) coupled with energy dispersive X-ray (EDX) analysis, X-ray diffraction (XRD), Fourier transform infrared (FTIR), UV-Vis and Raman spectroscopies. It was also investigated how mixing these transition metal oxides influenced their electrochromic properties.

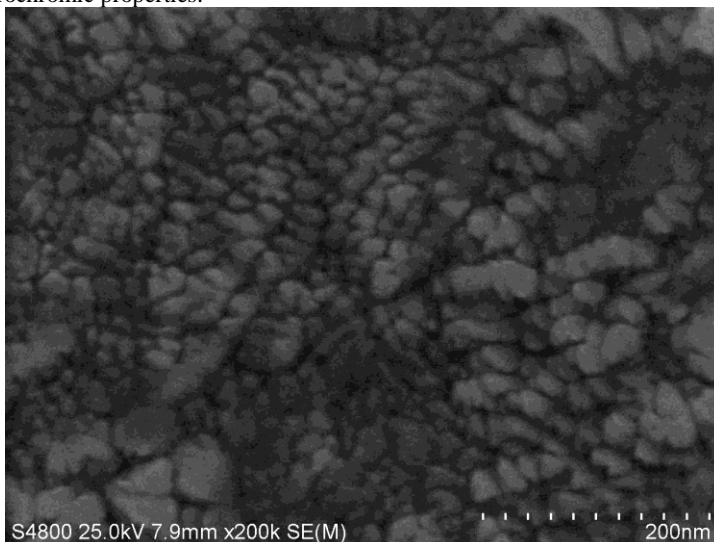


Fig. 1. SEM image of a  $\text{Mo-WO}_3$  thin film deposited by CVD at 200 °C.



## CHROMOGENIC SMART METAL OXIDE FILMS AND HOW INERA PROJECT HELPED BUILDING UP INTERNATIONAL RESEARCH TEAM FOR THEIR CHARACTERISATION

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During the Mobility visit of scientists from INERA Working Group 3 (Gesheva, Ivanova, Bodurov, CL SENES-BAS) in Uppsala University, Angstrom Laboratory, besides discussions and seminars, technological work was done. Dr. Miguel Arvizu, and G. Bodurov deposited thin films by reactive DC magnetron sputtering utilizing W and Mo targets and various oxygen gas-flows. The substrates used were glass covered with  $\text{In}_2\text{O}_3$ : Sn (ITO), 40 ohm/sq resistance.  $\text{WO}_3$  and  $\text{MoO}_3$ , and three different stoichiometry mixed metal oxide films were prepared. Mobility visit in the same Laboratory of docent Yordan Marinov from the Liquid Crystal Laboratory (ISSP-BAS) contributed to the utilization of INERA Impedance Spectrometer for voltammetric and impedance properties of the deposited oxide films. Helped by docent Popkirov (CL SENES), a three-electrode voltammetric measurements system was utilized. The films of  $\text{WO}_3$  exhibited good repeatability during cycling with insertion and extraction of Li ions, while the mixed films exhibited slight change in the shape and space of the curves. Impedance spectra reveal that the  $\text{WO}_3$  exhibit higher relaxation frequency (above 1 MHz) in comparison with the mixed W/Mo film, and higher starting frequency of the diffusion region. The mixed films demonstrated higher value of charge transfer resistance, 152 vs. 127 ohms/cm<sup>2</sup> for  $\text{WO}_3$ . Results show that the progress of ion insertion into the film for both cases leads to decrease of the diffusion line slope. Thus, the diffusion line is approaching 45° of slope which corresponds to standard diffusion.

Films thickness, determined in Angstrom laboratory by profilometer is around 300 nm. Utilizing the new INERA Ellipsometer, measurement (performed by INERA postdoctoral student Dr. Terzijska) of the films thickness was precisely made. With increasing of Mo content, the film thickness increases to 306 nm for the  $\text{W}_{0.7}\text{Mo}_{0.3}\text{O}_3$ , and to 309.8 nm for  $\text{W}_{0.86}\text{Mo}_{0.14}\text{O}_3$ .

The Raman spectra measurements were performed by prof. Abrashev on LabRAM HR Visible micro-Raman spectrometer. Peaks characteristic for monoclinic  $\beta$ - $\text{MoO}_3$  and orthorhombic  $\alpha$ - $\text{MoO}_3$  suggest that the amorphous  $\text{MoO}_3$  film exhibits a local order similar to that of monoclinic and orthorhombic phase. The Raman spectra of  $\text{WO}_3$  and the mixed films display strong lines, attributed to the stretching vibrations of  $\text{WO}_3$ .

AFM observations initiated by postdoctoral INERA employed student Dr. Stefan Boiadjev were performed with a Nanosurf FlexAFM in the Department of Inorganic and Analytical Chemistry, Budapest University of Technology and Economics. Results show that the film surfaces are characterized by irregularly distributed domed crystallites. The 3D topography of the mixed  $\text{W}_{0.92}\text{Mo}_{0.08}\text{O}_3$  film with phase contrast imaging (marked in different colors) allowed detecting regions with different compositions on the film surface.

As a result, a common paper is written, with 14 coauthors from 6 scientific organizations, two from abroad.