

LIV Zakopane School of Physics

International Symposium

BREAKING FRONTIERS: submicron structures in physics and biology

 $\begin{array}{l} {\rm May} \ 21^{\rm st}-25^{\rm th}, \ 2019 \\ {\rm Zakopane, \ Poland} \end{array}$

Organized by



The Henryk Niewodniczański Institute of Nuclear Physics Polish Academy of Sciences Editors: Wojciech M. Kwiatek Marta Marszałek Paweł Sobieszczyk

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Conference Timetable

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SATURDAY 25^{th} May 2019

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POSTER SESSION 22^{th} May 2019, 19.00

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Invited talk, Tue./19:00

Topological semimetals

D. Kaczorowski

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Initiated by the discovery of topological insulators, topologically non-trivial matter, especially topological semimetals (TSM), has emerged as a new frontier in the field of quantum materials. Among various TSMs, one recognizes Dirac semimetals (DSM) that exhibit accidental band touching between conduction and valence bands, protected by time-reversal and inversion symmetry, as well as Weyl semimetals (WSM), in which one of those symmetries is broken, and single-degenerated band crossings with linear dispersion possess non-zero chiral charge. Another subgroup of TSMs consists of nodal-line semimetals (NLSM) with Dirac band crossings forming a closed trajectory in momentum space, protected by mirror, glide, or screw symmetries. The presence of nearly massless quasiparticles near chemical potential gives rise to unique transport properties of TSMs, like ultra-high charge carrier mobility, non-trivial Berry phases, huge non-saturating magnetoresistance (MR), weak antilocalization effect, chiral magnetic anomaly (negative longitudinal MR, planar Hall effect, angular narrowing of longitudinal The most intriguing physical phenomena observed in TSMs not MR), etc. only provide excellent tests for fundamental theories, but also promise a wide range of possible applications in low-power spintronics, optoelectronics, quantum computing and green energy harvesting.

Here, in our brief introduction to the blooming field of TSMs, we first recall some basic theoretical concepts, and then confront them with our recent accomplishments in experimental observations of Dirac/Weyl states via angle-resolved photoemission spectroscopy (ARPES) and comprehensive studies on anomalous low-temperature electronic transport behaviors in a few different DSM, WSM and NLSM materials.

Acknowledgment: Part this research was supported by the National Science Centre (Poland) under MAESTRO grant no. 2015/18/A/ST3/00057.

Invited talk, Wed. /08:30

Fundamentals and Applications of Surface-Enhanced Raman Spectroscopy (SERS)

M. R. Lopez-Ramirez, J. C. Otero, J. Soto, J. L. Castro, J. F. Arenas

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When a molecule is adsorbed on some metallic nanostructured surfaces such as silver, copper or gold, it can undergo an enormous enhancement of the Raman signal giving rise to the so called Surface-Enhanced Raman Scattering (SERS). The high sensitivity of this effect allows an accurate structural study of adsorbates at very low concentrations. The SERS effect has historically been associated with the substrate roughness on two characteristic length scales. Surface roughness on the 10 to 100 nm length scale supports localized plasmon resonances which are considered as the dominant enhancement mechanism of SERS (Electromagnetic Enhancement Mechanism: SERS-EM). It is usually accepted that these electromagnetic resonances can increase the scattered intensity by an average factor of ca. 10^4 to 10^7 .



Figure 1. SERS effect.

A secondary mechanism often thought to require atomic scale roughness is referred to as Charge Transfer (CT) Enhancement Mechanism (SERS-CT). This mechanism involves the photoinduced transfer of an electron from the metal to the adsorbate or vice versa and involves new electronic excited CT states which result from adsorbate-substrate chemical interactions. It is also estimated that such SERS-CT mechanism can enhance the scattering cross-section by a factor of ca. 10 to 10^2 . These two mechanisms can operate simultaneously, depending on the particular systems and experimental conditions, making difficult to recognize each one and to estimate their relative magnitude in a particular spectrum.⁽¹⁾ From the point of view of the metal nanostructures, electromagnetic interaction of light with nanoscale metals can generate collective oscillations of conduction electrons generally known as localized surface plasmon resonances (LSPRs) which constitute the basis of new fundamental research and applications, i.e. catalysis, plasmonic solar cells or nanodevices for bio-applications. Additionally, Raman scatterers molecules located at the interparticle junctions may experience SERS enhancement that exceeds that of the isolated nanoparticles by several orders of magnitude enabling the detection of single molecules. $^{(2)}$

- ⁽¹⁾ M.R. Lopez-Ramirez, D. Aranda Ruiz, F.J. Avila Ferrer, J.F. Arenas, J.C. Otero, J. Soto, J. Phys. Chem. C 120 (2016) 19322–19328.
- ⁽²⁾ K. Kneipp, Y. Wang, H. Kneipp, L. T. Perelman, I. Itzkan, R. Dasari and M. S. Feld, Phys. Rev. Lett., 78, (1997) 1667–1670.

Invited talk, Wed./09:00

Magnetic nanostructures: from magnetic simulations to sensor and storage applications

D. Suess

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Within the talk I will review our activity on magnetic and spintronic applications. In the first part of the talk, our research on state of the art heat assisted recording will be presented that is done in cooperation with Western Digital and Seagate. Here, fundamental problems in laser assisted recording (heat assisted recording) such as noise due to the elevated temperature will be discussed. Solutions to increase data density and noise that bases on multilayer materials with different Curie temperature will be presented.

A further part of the talk will be dedicated to the newest developments of the CD-lab "Advanced magnetic sensing and materials" with is done in cooperation with Infineon. One highlight that will be presented is the significant reduction of the noise in tunneling magnetoresistance sensors (TMR) that are used for speed wheel sensors for ABS systems in cars. The way from the idea of these new sensors to the development of a product that will enter the market in 2019 will be discussed (1). Finally, I will give a review about our activity in additive manufacturing. We developed magnetic filaments that can be used in a commercial 3D printers that allows to print polymer bonded NdFeB magnets. The used 3D printing system is also capable to extrude two different filaments, which allows a gradual change in magnetic properties. Hence, a continuous change from a magnetic material to a non-magnetic can be realized as function of space. This capability allows generating magnetic field profiles which are not possible with other methods. In order to fully make use of these new production flexibility advanced algorithm are required to determine the shape of magnet as well as the local magnetic properties to obtain the required and predefined magnetic field $^{(1,3)}$.

- ⁽¹⁾ Suess, Dieter, et al., Nature Electronics 1.6 (2018): 362.
- ⁽²⁾ Huber, C., et al., Applied Physics Letters 109.16 (2016): 162401.
- ⁽³⁾ Huber, Christian, et al., Scientific reports 7.1 (2017): 9419.

Invited talk, Wed./09:30

Ion beam patterning of magnetic landscapes and nanostructures

A. Semisalova

Helmholtz-Zentrum Dresden-Rossendorf, Dresden, Germany

Invited talk, Wed./10:00

Lithographically defined magnetic nanostructures for biomedical therapy and detection

<u>R. Cowburn</u>

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Magnetic materials are currently used in a number of biomedical applications such as therapy, diagnostics, separation and sorting, with hyperthermia therapy being the most well-known. To date most biomedical magnetism uses very simple magnetic materials - typically superparamagnetic iron oxide nanoparticles (SPION). This talk will describe a new approach in which physical vapour deposition (sputtering) combined with lithography is used to form large numbers of nanoand micro-structures across a silicon wafer, which are then released into solution to form a highly functional magnetic liquid⁽¹⁾. The advantage of this approach over SPION is that phenomena such as RKKY coupling, spin textures and interfacial anisotropy can all be used to make the magnetic properties of the liquid more advanced and therefore better suited to particular biomedical applications. In this talk we show how these advanced properties can be used to control the agglomeration of magnetic particles in liquid (a key problem in biomedical applications of magnetism) $^{(2)}$, can be used to treat glioblastoma brain tumours in mice with increased survival times of the animals $^{(3)}$ and can be combined with neural stem cells for targeted delivery $^{(4)}$.

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Invited talk, Wed./11:00

High-spatial-resolution laboratory X-ray bioimaging

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X-rays are an essential tool for biomedical research since it allows 2D and 3D imaging in intact thick objects with high spatial resolution. For many applications easy access and acceptable exposure times are of key importance. We have developed laboratory x-ray imaging methods that enable easy access and short exposure times: Water-window x-ray microscopy (XRM) gives tens-of-nm imaging in intact cells and a hard x-ray phase-contrast imaging for mm imaging in tissue or organs. In both cases novel high-brightness liquid-jet sources are key components for the systems. The Stockholm water-window XRM relies on a liquid-nitrogen-jet-target laser-plasma x-ray source which is combined with multilayer condenser optics, zone-plate imaging optics and cryogenic sample handling. The present microscope delivers 2D images in 10-20 seconds and allows repeated tomographic imaging with up to hundred projections during typically 1 hour total data acquisition time. Recent applications include imaging autophagy-relevant behavior of starving HEK cells, interaction between NK-cells and HEK target cells, and assessment of virus infection dynamics in amoebas.

The phase-contrast x-ray imaging relies on liquid-metal-jet sources and scintillator detectors in a magnifying scheme. The method allows observation down to cellular, and in some cases subcellular, detail within the context of the whole organ or whole animal. Recent examples include cellular detail in human coronary arteries and mummified finger tips, and subcellular muscle imaging in whole-body zebra fish.

Invited talk, Wed./11:30

Biophysical models of cell death and their role in tumor hadrontherapy

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Biophysical models can be of great help to shed light on the mechanisms leading from the initial interaction of ionizing radiation with biological matter to observable biological effects like DNA damage, cell death etc. Furthermore, such models allow making predictions for those scenarios where the experimental data are scanty or absent.

This lecture will describe and discuss examples of modelling approaches related to radiation-induced cell death, which is extremely relevant for cancer therapy, where the main objective is to kill tumour cells. The attention will be focused on the different model assumptions and parameters, the comparisons with experimental data, and the possible implications in terms of biophysical mechanisms and/or applications for cancer hadron therapy. In particular, a model developed in Pavia (called BIANCA, BIophysical ANalysis of Cell death and chromosome Aberrations e.g.^(1,2)) will be presented, including the recent production of a radiobiological database that, following interface to a MC radiation transport code (e.g. FLUKA) or a TPS, can predict cell death and chromosome damage along hadrontherapy beam profiles. Comparisons will be also shown with other models including the Local Effect Model (LEM), which is currently used for the treatment planning of patients irradiated by C-ions in Germany and at CNAO in Pavia, Italy.

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Invited talk, Wed./12:00

Carbon based materials for medical applications

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Carbon materials are an interesting group of materials that are also important in medicine. The variety of forms of synthetic carbon materials and the various properties associated with them make that these materials are interesting for applications in area of medicine. Among these materials, carbon fibers can be indicated as a reinforcing phase in the composites used to reconstruct the bone tissue or as a kind of prostheses or orthoses used in fractures of the limbs. Also known in medicine are the pyrolytic and diamond-like carbon layers used on the elements of implants intended for contact with blood. In recent years, carbon nanoforms such as carbon nanotubes (CNTs), graphene (G) or carbon nanofibers (CNFs) have also become popular in medicine. Carbon nanotubes are the best investigated carbon nanomaterials used for a wide range of biological applications. These materials are taken into account in drug delivery systems, as potential scaffolds for tissue regeneration, biosensors, elements for cancer diagnosis and treatment etc. Carbon nanostructures have unique mechanical, electrical and physicochemical properties, and their shape (CNTs and CNFs) is similar to neurites. They are also the subject of growing interest in biological applications which recently have extended into the area of electrodes for nerve tissue stimulation. CNTs have successfully proved to stimulate neurite outgrowth, improve neuronal performance and recording, neuron differentiation, boost neuronal electrical signalling and work as a substrate for the growth of neurons. The main aim of the work will be to present areas of application of carbon materials in medicine, with particular emphasis on carbon nanomaterials as new generation materials for stimulation of bone, muscle and nerve tissue cells. The aspect of potential cytotoxicity of carbon nanomaterials in vitro and in vivo conditions will also be discussed.

Acknowledgements: This study was funded by the National Science Centre (Grant No. UMO-2013/11/D/ST8/03272).

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Contributed talk, Wed./12:30

Influence of stabilizer on the drug/metal nanocarrier interaction: SERS and AFM - IR studies

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In this analysis, we present the spectroscopic evaluation of erlotinib and gefitinib interaction with potential metal nanocarriers. Both drugs are known as a reversible and competitive inhibitor of the tyrosine kinase domain of the epidermal growth factor receptor (EGFR). Due to their antitumor activity, these drugs are applied in the target therapy for patients suffering from non - small cell lung cancer (NSCLC)^(1,2).

Surface - enhanced Raman spectroscopy (SERS) technique was applied to characterize structural geometry of the studied drugs after their adsorption onto the different types of silver and gold colloidal nanoparticles stabilized using various agents. We have discussed the influence of the applied stabilizer on the observed adsorption pattern. Additionally, the technique combined atomic force microscopy with infrared spectroscopy (AFM-IR) allow us to indicate orientation of the particular functional groups onto the used metal surfaces in nanoscale spatial resolution. The detected spectral changes upon two orthogonal polarization modulation reveal the crucial relationship among the state of the incident light polarization and the relative infrared band intensities⁽³⁾.

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Bruker, Wed./12:45

Latest advances in nanoscale IR spectroscopy and imaging

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For the last few decades the rapid growth in the field of nanoscience and technology has led to the development of new characterization tools for nanoscale materials. Traditional IR and Raman spectroscopy and imaging offers excellent chemical insights, however, the spatial resolution is limited by the optical diffraction limit (~wavelength/2). Although, recent Super-resolution microscopy techniques offer superior spatial resolution, they are primarily implemented in fluorescence imaging, hence needs external fluorophore tag for detection. Alternatively, nanoscale IR spectroscopy/imaging offers a "tag free" spectral detection with high spatial resolution beyond optical diffraction limit (2-5 microns) by exploiting an AFM probe to detect either photothermal expansion force (PTIR) or near field scattered IR light (sSNOM).

Recent developments in PTIR and sSNOM technology have significantly augmented the speed and spatial resolution for chemical analysis. One of the new developments (Tapping AFM-IR) allows acquisition of IR images at a specific absorption band simultaneously with sample topography and nano-mechanical properties, providing a complete set of topographical, chemical and mechanical insights with <10 nm spatial resolution. These high-resolution measurements are currently accompanied by high speed tunable laser enabling fast point spectral acquisition (1-2 ms/spectrum) leading to hyperspectral data cube for rigorous statistical analysis similar to Chemometrics applications.

In this presentation, we will highlight the technical background and applications of these emerging technologies in different fields, e.g., nanomaterials, life sciences, polymers, microelectronics etc. Contributed talk, Wed./14:00

Composition-dependent THz emission of spintronic Tb_xFe_{1-x}/Pt layers

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Bi-/multilayer structures of ferro-/ferrimagnetic (FM) and nonmagnetic (NM) metals have been shown to be THz emitters when excited by femtosecond laser pulses. ⁽¹⁻³⁾ Amplitude and frequency of the emitted THz radiation depend on the film thickness, the electric and magnetic properties of the FM layer, and the spin-Hall conductivity of the NM layer and can therefore be tuned by changing the composition of the used layer stack. ⁽⁴⁾ Here we report on the THz emission of ferrimagnetic Tb_xFe_{1-x} ($0 \le x \le 1$) combined with Pt. All films were magnetron sputter deposited at room temperature. The dependence of the THz radiation on the sample magnetization has been investigated with respect to the composition of the ferrimagnetic layers.

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Contributed talk, Wed./14:20

Exchange Bias in CoO/Fe(110) Bilayers: a Ferromagnet Drives an Antiferromagnet

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The Ferromagnet/Antiferromagnet (AFM/FM) bilayers that display the exchange bias (EB) effect are subjected to intensive material research. In a commonly accepted picture, the AFM, considered as rigid due to its high anisotropy and magnetic hardness, controls the magnetic properties of the FM. We show that this AFM-FM master-slave hierarchy is not generally valid, and that the influence of the FM to the magnetic anisotropy (MA) of neighboring AFM must be considered. Our computer simulation and experimental studies of EB in epitaxial CoO/Fe(110) bilayer show that the FM layer with strong uniaxial magnetic anisotropy decides on the interfacial spin orientations of the neighboring AFM layer and rotates their easy axis. This effect, directly confirmed by XMLD measurements performed at the XAS end-station in SOLARIS facility, has strong feedback on the EB effect experienced by the FM layer (1).

⁽¹⁾ M. Ślęzak, T. Ślęzak, P. Drożdż, M. Matlak, K. Matlak, A. Kozioł-Rachwał, M. Zając, J. Korecki Scientific Reports 9 (2019) 889

Contributed talk, Wed./14:40

Magnetic nanostructures patterned in (Ga,Mn)(Bi,As) thin films for memory applications

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Modern problems require modern solutions - on a quest for new, smaller and more efficient materials, that are both interesting from the point of spintronic applications (1,2) and for physical phenomena investigations, our team focused on thin films of ternary (Ga,Mn)As and quaternary (Ga,Mn)(Bi,As) dilute magnetic semiconductors (DMS). The MBE-grown films excel in good crystalline quality, confirmed with high resolution X-Ray diffractometry and transmission electron microscopy (TEM), have relatively high Curie temperature and well-defined, dependent on the growthinduced strain, magneto-crystalline anisotropy, as verified by superconducting quantum interference device (SQUID) magnetometry. Within the presentation we'd like to show ring- and crossshape nanostructures, patterned with the use of electron-beam lithography in the DMS films containing 6% Mn and 1% Bi. Using those examples we demonstrate how to realize a concept of magnetic memory based on the magnetic domains utilizing the interplay between the original crystalline and the shape-dependent magnetic anisotropy. For the two types of nanostructures their resistance, measured under a weak in-plane magnetic field at low temperatures, displays hysteresis-like behaviour, controlled by rearrangement of domain walls in the nanostructures, which could be utilized in a new class of nonvolatile two-state memory cells.

This work was supported by the Polish National Science Centre under grant UMO- $2016/23/{\rm N}/{\rm ST3}/03501$ Preludium.

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Contributed talk, Wed./15:00

Magnetic anisotropy and magnetization reversal mechanisms of nanoporous Co/Pd thin films

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Nanstructurized magnetic thin lms exhibit very different properties from those of continuous lms connected with the in uence of morphology (size, shape, and distribution of structures) on the magnetic anisotropy and demagnetization processes in the porous films. Nanoporous lattice of holes, called antidots, were fabricated by deposition of Co/Pd multilayers on anodized aluminum oxide (AAO), where the pores are located in the middle of hexagonal packed hemispherical deepenings. The present work is focused on the magnetic Co/Pd multilayers (ML) deposited on nanoporous Al_2O_3 templates with different pore diameters (10-35 nm).

The studies concern the properties of as deposited films and annealed in vacuum at 300°C. To determine the contribution of pore morphology to magnetic properties of the system, Co/Pd (ML) on flat Si substrate was also prepared. SEM imaging confirmed nanoporous morphology of the films before and after annealing.

All nanoporous films preserved perpendicular magnetic anisotropy. However, after annealing a twofold decrease of coercive field was detected. MFM imaging of Co/Pd multilayers and CoPd alloy compared to continuous films showed more complex magnetic contrast with smaller magnetic domains. The difference in MFM images can be explained by the pinning effect of the magnetic domains on the pore borders and edges of pore cells. Magnetic reversal mechanism of continuous Co/Pd multilayers is based on domain-wall motion. For nanostructured films magnetic reversal mechanism significantly changed and behave like coherent rotation model.

Contributed talk, Wed./15:20

Magnetization reversal mechanism and domain structure in nanopatterned thin films with perpendicular magnetic anisotropy

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Fabrication and modeling of patterned thin films with perpendicular magnetic anisotropy rise great interest due to their wide applications in magnetic storage, sensors and magnonic crystals. A good representative of such systems are well-ordered arrays of magnetic antidots and dots based on Co/Pd multilayers, where magnetic reversal mechanisms strongly depend on the array geometry ^(1,2). We attempt to understand and reproduce the observed magnetic properties and domain structure appearing in the arrays by micromagnetic simulations performed using Mumax3 software ⁽³⁾. In particular, changes in coercivity field, magnetic anisotropy constant and magnetic domain arrangement were studied and correlated with symmetry and size of nanostructures. The calculations show how edge effects, defects and inhomogeneity affect magnetization reversal and domain wall pinning mechanism, which helps to design similar patterned systems with the specific magnetic properties.

Acknowledgments: The numerical simulations were supported in part by the PL-Grid Infrastructure.

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Contributed talk, Wed./15:40

Towards magnetic 1D nanostructures - magnetic field as a growth parameter

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Since ancient times, the magnetic field has been recognized as either an intrinsic material property or a parameter which describes the magnetic interactions between materials. However, it has been already proven that the magnetic field can also act as a reaction parameter, similar to conventional reaction conditions i.e. temperature, pressure, time, and chemical additives. In fact, such processes are known as a magnetic-field-induced synthesis and they lead to the formation of various magnetic wire-like nanostructures⁽¹⁾.

Most of the scientific works about the magnetic-field-induced processes describe the preparation of metallic nanowires like: iron nanowires⁽²⁾, cobalt nanowires⁽³⁾ or nickel nanowires⁽⁴⁾. Very few publications, which show how to manufacture bimetallic wire-like structures, have been published so far. This is associated with the fact that the synthesis of such materials is much more complicated than the simple metallic structures. Nevertheless, the novel magnetic-field-induced procedures leading to the formation of bimetallic iron-nickel nanochains are shown in this work. Besides that, the investigations of their morphological and structural properties using a scanning electron microscopy (SEM), a transmission electron microscopy (TEM), a powder X-ray diffraction (XRD), as well as magnetic properties carried out by a vibrating sample magnetometry (VSM) are also provided herein.

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Contributed talk, Wed./16:30

Slow magnetic relaxations in Dy (III) single molecule magnet induced by an applied static magnetic field

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Molecular magnetism has introduced a vast variety of novel materials that are currently of great interest to physicists and chemists around the world. Because of their unique properties, molecular magnets find potential applications in spintronics, magnetic recording, magnetic refrigeration, or photomagnets switched by the light. They exhibit a broad variety of structures, often with a low dimensionality of the coordination network that fosters the occurrence of magnetic relaxation phenomena. Identifying and understanding the processes involved in magnetic relaxation may be a key step towards the development of new technology.

Analyzed compound $[Dy^{III}(Zn^{II}L)_2]CF_3SO_3$ is a Single Molecule Magnet (SMM) crystallizing in the trigonal system (space group: R32). The compound does not exhibit any phase transition to a long-range magnetically ordered state in the studied temperature range of (2 K to 300 K). Magnetic properties of one single crystal were carried out in two sample orientations in regard to an applied external magnetic field. The strong magnetic anisotropy with an easy axis [001] perpendicular to the sample surface was observed. Magnetic relaxations appear only in [001] direction with two relaxation processes, slow and fast, that show a strong dependence on static magnetic field and unusually weak temperature dependence. Eventually, two relaxation processes were identified that comprise the slow process: quantum tunneling in low magnetic fields range and direct process accompanied by phonon bottleneck phenomenon in higher magnetic fields.

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Contributed talk, Wed./16:50

Study of magnetocaloric effect in the electrodeposited thin films of Prussian blue analogues

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Extensive research over the past decade has focused on the design and characterization of the novel molecular materials demonstrating unusual properties which are not observed in the conventional metallic magnetic materials, i.e. low density or sensitivity to external stimuli such as light, pressure, and temperature. Among molecular magnets, the key compounds are Prussian blue analogues (PBAs) displaying many fascinating functional properties, such as photomagnetism, ionic conductivity or sorption capacity. An additional advantage of PBAs is the possibility of fabrication of these materials as objects of various dimensions: nanoparticles, nanowires, and thin films.

In this report, we undertake the challenge of combining the materials' functionality with the reduced dimensionality and present the study of the magnetocaloric effect in PBAs thin films. The thin films of general formula $M_3[Cr(CN)_6]_2 \cdot nH_2O$, where M=Fe, Cr, were synthesized by electrochemical deposition. Fe₃[Cr(CN)₆]₂ · nH₂O shows a sharp phase transition to a long-range ferromagnetically ordered state at $T_c = 24$ K. $Cr_3[Cr(CN)_6]_2 \cdot nH_2O$ is a ferrimagnet with $T_c = 225$ K. For both compounds, the films oriented parallel to the direction of the external magnetic field yield different magnetic response than the films oriented perpendicular to the field. This anisotropic behaviour can be explained by the geometry of the demagnetization factor. Besides the analysis of the change of magnetic entropy as a function of temperature and its variation upon the rotating the sample from in-plane to out-of-plane orientation, we have studied the scaling behaviour of MCE for the sample in both positions.

Contributed talk, Wed./17:10

A novel detector based on the vortex Mott insulator-to-metal transition

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The terahertz (THz) region of the electromagnetic spectrum is often described as the final unexplored area of spectrum. In this energy region, different physical phenomena such as the phonon dynamics and the bound states of quantum wells can be investigated. However, THz instruments and detection capabilities are limited in comparison with the adjacent IR domain. Hence, construction of novel detectors with enhanced capabilities create possibilities in many fields from the solid state (phonon dynamics), astrophysics (galactical formation and evolution) to particle physics (axions and cold dark matter) investigations.

An array of superconducting proximity islands has been shown to be highly tunable by electric, thermal and magnetic fields ^(1,2). Indeed, a small change in the electric, thermal and magnetic field can tune the system from a vortex Mott insulator to a vortex metal. A vortex Mott insulator occurs in a type II superconductor if the density of the superconducting vortices matches the density of the pinning sites ^(2,3), however only in the array of superconducting island, free from the disguising effect of disorder, the dynamic state has been unveiled. Based on the non-bolometric effects associated with the occurrence of non-equilibrium phenomena in superconducting networks⁽⁴⁾, we will discuss in this contribution the possible applications of this array for a conceptually new particle/radiation detector with an extremely high-energy resolution (proportional to \sqrt{E}). The system we designed and realized consists of an array of about 90000 Nb superconducting islands symmetrically deposited on a non-superconducting support in an area of $80 \times 80 \ \mu m^2$ and with a period of 270 nm, an island diameter of 220 nm and thickness of 45 nm. The array is under test at the COLD laboratory in Frascati and shows a critical superconducting temperature of 7.9 K while, the universal scaling properties of the current and magnetic of the vortex Mott insulator dynamic transition are in agreement with previous measurements^(1,2). Based on these promising results, we will present the integration of the array in the newly proposed detector, discussing the challenges and the solutions we will consider to optimize the performance.

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INVITED TALK, THU./15:00

Femtosecond spectroscopy and diffraction in applied science at the ELI Beamlines facility

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This presentation introduces the activities of the research programme for Applications in Molecular, Biomedical and Material (MBM) science at the ELI Beamlines (ELI BL) facility in the Czech Republic. The MBM research programme develops methods for time resolved studies (spectroscopy, diffraction and imaging) of ultrafast phenomena in physics, chemistry and biology utilizing pulsed lasers and laser driven X-ray sources. The ELI BL facility is part of a European Strategy Forum for Research Infrastructures (ESFRI) plan to build a new generation of research facilities in new EU member states and offer these to an international user community. The scientific activities at ELI BL will be based on the utilization of four unique short pulse lasers. Each one with a unique combination of pulse profile, repetition rate and intensity. Part of the ELI BL mission is to develop a new generation of laser driven light sources for ultrashort pulses covering the VUV to gamma-ray energy range based on plasma effects in gases and solids as well as relativistic electron acceleration. All sources have the potential to be used in combination with beams split off from their corresponding drive lasers for pump-probe experiments. In contrast to the situation at accelerator based light sources, like synchrotrons and FELs, the fact that the pump pulse can be split off from the same laser pulse that generates the X-ray pulse provides an intrinsic synchronization between the pump and the probe pulses.

Here we focus mainly on the scientific applications of the Higher Harmonics Generation (HHG) source and Plasma X-ray Source (PXS) driven by a high power kHz laser for which the MBM research programme develops experimental stations for AMO science and Coherent Diffractive Imaging, time resolved spectroscopic ellispometry as well as time resolved X-ray diffraction, spectroscopy and pulse radiolysis. These X-ray stations are complemented by a very advanced experimental environment for time resolved optical spectroscopy (including transient optical absorption, fs Stimulated Raman Scattering, 1 and 2D IR spectroscopy and spectroscopic ellipsometry). ELI Beamlines will offer a complementary set of X-ray, VUV and advanced optical techniques in one easily accessible location. In combination with advanced sample preparations laboratories (in particular for biosamples), this will open up new possibilities for or the study of complex ultrafast phenomena in physics, chemistry and biology. INVITED TALK, THU./15:30

Quantum control and ultrafast catalytic studies at Extreme Light Infrastructure (ELI)

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Currently available spectroscopy instrumentation delivers ultrafast methods of tracking chemical reactions in real time. This is achieved in the so called pumpprobe approach⁽¹⁾ where the target material is first irradiated with a pump pulse initiating the reaction and after a short delay (femtoto picoseconds) with a probe pulse used to investigate the target's state. Consecutive irradiation with pump and probe pulses at different delay times allows time-resolved study of the pump pulseinitiated reaction.

We work on application of the optical pump-X-ray probe methodology to catalytic reactions. In our approach a pulse shaper is used to modify the optical pump pulse in order to control the material's surface potentials and consequently to direct the catalytic reaction (the so called quantum control). The desired pulse shape will be established with a setup similar to that of Nuernberger et al.⁽²⁾ where the modulated laser pulse ionizes and initiates reaction in the studied material. The reaction products are directly analysed by the time-of-flight mass spectrometer (TOF-MS) and the results are processed on-the-fly by a learning single-objective algorithm which controls the pulse shaper. In our setup's design, however, the pump pulse is split into two, one for quantum control and another for ionization of the neutral product molecules. Also, we will use a multi-objective genetic algorithm (MO-GA) with a feedback $loop^{(3)}$ which will allow varying systematically the pulse's duration, phase, amplitude and energy-scale and will help finding the global extrema instead of the local ones. We expect that these two modifications will appreciably increase the tool robustness and reproducibility. The X-ray probe pulses will allow tracking the catalysis by investigating the catalytic active site's valence and conduction bands with resonant X-ray emission spectroscopy (RXES)⁽⁴⁾ and high energy resolution off-resonant spectroscopy (HEROS) $^{(5)}$. RXES will give insight into the density of occupied electronic states in the valence band and the density of unoccupied states will be studied with HEROS. RXES and HEROS measurements will be done on the shot-to-shot basis with a von Hámos geometry-based spectrometer⁽⁶⁾. Application of the X-ray spectroscopy methodology will deliver information of the catalytic active site during the chemical bond formation and breaking.

Currently, at the Extreme Light Infrastructure (ELI) the pulse shaping setup is being developed and the time-of-flight mass spectrometer tested. The ELI's E1 experimental hall providing a number of pump beams and equipped with a plasma X-ray source (PXS), currently under development, will serve in the future for quantum control and pump-probe experiments.

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INVITED TALK, THU./16:00

Tracking light-induced ultrafast transformations of transition metal complexes

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Photo-induced transformations of molecular systems are ubiquitous in various branches of chemistry, physics, molecular biology, and materials science. They are essential in photosynthesis and photocatalysis, and have high potential for molecular storage or switching devices, and light-harvesting systems. In order to design better performing functional molecules with ligand engineering, understanding the elementary steps and the formation of transient species in related molecular reactions, phase transitions or biochemical function is inevitable. However, the traditional tool set of pump-probe experiments has several limitations, preventing us from capturing many relevant aspects needed to fully understand the underlying ultrafast dynamics. Exploiting hard X-ray techniques to probe the ultrafast dynamics in pump-probe experiments can provide us with novel element sensitive insights⁽¹⁾. The intense femtosecond X-ray pulses of X-ray free electron lasers permit us to exploit the X-ray spectroscopy tools with the appropriate time resolution, offering direct access to the changes in the charge, spin and nuclear degrees of freedom during the elementary physical processes of a chemical reaction, photophysical transformation, or biological function $^{(2)}$. Combining spectroscopy with X-ray diffuse scattering allows us to simultaneously address both the electronic and structural dynamics of the molecule in the solvent cage, as well as the relaxation of the product molecule and the energy transfer to the solvent $^{(3)}$. The development in time resolution made it possible to separate the details of these processes, and with the help of quantum chemistry and quantum dynamics the mechanisms are becoming fully understood⁽⁴⁾. Results obtained on light-excited transition-metalbased model systems for photo-switchable or light-harvesting functional molecules, as well as ligand exchange reactions will be shown as examples.

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Contributed talk, Thu./16:50

Magnetic properties characterization of Fe-based amorphous ribbon after interference pulsed laser heating

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Influence of pulsed laser interference heating process on magnetic properties and structure of ironbased amorphous ribbon are reported. Laser interference heating allows creating periodically placed laser heated micro-areas. In the laser affected microareas, structure and magnetic properties changes occur. To compare obtained results the samples after conventional crystallization were prepared by annealing at 600°C. Microstructure characterization by electron microscopy showed that the laser beam energy cause the partial crystallization of amorphous material. Partial crystallization affect magnetic properties of material. Magnetic hysteresis loop measurement by SQUID magnetometer showed the difference in saturation magnetization with unchanged remanence. Magnetization of material in single laser heated microareas was determined by magnetic force microscopy. Investigations showed the differences in magnetic structure of amorphous material and laser affected material.

The work was supported by National Science Centre (NCN) of Poland (contract number: OPUS 10, UMO-2015/19/B/ST8/01070)

Contributed talk, Thu./17:10

The Z-dependence for the off-resonant excitations cross-sections for 3D elements

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The X-ray off-resonant excitations, or Resonant Raman Scattering (RRS), is an inelastic process observed experimentally for the first time in 1974⁽¹⁾, and explained shortly after⁽²⁾. The process involves the core-shell electron excitation with photon energy lower than the ionization threshold of given element. The mechanism is possible thanks to the virtual intermediate state that is mediating the electron excitation above Fermi level with the expense of the X-ray fluorescence photon energy. Physical properties of the virtual state are important due to the connection with nonlinear processes driven by a the same intermediate state, i.e. sequential two-photon absorption (TPA). As a consequence, the cross-sections relations between the one photon off-resonant excitation and the two-photon absorption can be studied and it is possible to derive the cross-sections value for TPA based on the one-photon interaction data⁽³⁾.

For many years the off-resonant excitation were observed by use of monochromatized radiation from X-ray tubes $^{(1,4,5)}$ or synchrotrons $^{(6-9)}$. Yet, the cross-sections values were determined so far only for handful of elements, usually by means of low energy resolution measurements. Herein we report the determination of the cross-section values for elements from 3d group, based on the measurements performed at synchrotron with use of high energy resolution X-ray spectroscopy. Based on the experimental data, we estimate the cross-sections dependence on the atomic number. The data suggest the quadratic dependence of the off-resonant cross-section values on the atomic number of element, which is similar to the non-resonant excitations cross-section dependence as well as the dependence of the core-hole lifetimes $^{(10)}$. Based on the obtained results, we will discuss expected dependences for cross-sections for nonlinear two-photon absorption mechanisms and examine the influence of the intermediate state lifetime. Authors would like to acknowledge National Science Centre, Poland (NCN) for partial support under grant no. $2015/19/{\rm B}/{\rm ST2}/00931$

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Contributed talk, Thu./17:30

Tracking electron configuration of tungsten during thermal oxidation

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Tungsten (VI) oxide (WO_3) is an important multifunctional material with appealing chemical, electrical, optical and structural properties. Due to its electrochromic and photochromic properties, i.e. reversible colour change upon application of a suitable electric potential or irradiation with light, tungsten trioxide has been used in electronic displays, smart windows and sunroofs⁽¹⁾. Moreover, WO_3 is a n-type semiconductor with a band gap of Eg = 2.5-2.8 eV, which favours visible light absorption ($\lambda \leq 470 \text{ nm}$)⁽²⁾. Thus, tungsten (VI) oxide is considered as a promising candidate for photocatalytic water splitting into hydrogen fuel and molecular oxygen. Tungsten (VI) oxide crystals are formed by corner and edge sharing of perovskite-like $[WO_6]$ octahedral building blocks and have various phases, including: monoclinic II (ϵ -WO₃), triclinic (δ -WO₃), monoclinic I (γ -WO₃), orthorhombic (β -WO₃) and tetragonal (α -WO₃)^(1,3). Recent studies showed that the photocatalytic efficiency of WO_3 is a compromise of the band gap, crystal phase, morphology and the oxidation state $^{(4)}$. Till date, several methods such as thermal evaporation, chemical vapour deposition, electro-spinning, sol-gel, chemical bath deposition, hydrothermal and templatedirected synthesis have been used to prepare the oxide in the most varied morphologies, dimensional arrangement and crystal structures. Possibly the simplest methodology to form WO_3 on W-foil is the thermal oxidation of the metallic substrate. Although substantial experimental work has been devoted to understand oxidation mechanism of tungsten, theories and the current understanding are still limited $^{(5)}$. This is in great extent due to the complexity of the oxidation mechanisms as well as the wide variety of oxides formed during oxidation.

In the presented work, we have investigated changes in the W electronic structure during thermal oxidation of the metallic tungsten to tungsten (VI) oxide. The process was followed by in situ X-ray spectroscopy methods that enabled us to study real time changes in the unoccupied and occupied electronic states of the material by a combination of high-resolution X-ray absorption (see Fig. 1) and X-ray emission spectra. Application of the high energy resolution spectroscopy allowed us to detect splitting of W 5d states by the ligand field into t_{2g} and e_g orbitals. From measured data we derived contributions of atomic orbitals to the valence and conduction band together with a quantitative analysis of ligand field splitting.



Figure 1. Electronic structure changes in the conduction band of W induced by metal to metal-oxide transition.

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Contributed talk, Thu./19:00

Self-assembly of highly sensitive 3D angular encoders

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Novel robotic, bioelectronic and diagnostic systems require a variety of compact and high performance sensors. Among them, compact 3D vector angular encoders are required to determine spatial position and orientation in a three-dimensional environment. However, fabrication of 3D vector sensors is a challenging task associated with time consuming and expensive, sequential processing needed for the orientation of individual sensor elements in 3D space. Here, we demonstrate the potential of 3D self-assembly to simultaneously reorient numerous giant magnetoresistive (GMR) spin valve sensors for smart fabrication of 3D magnetic angular encoders. During the self-assembly process, the GMR sensors are brought into their desired orthogonal positions within the three Cartesian planes in a simultaneous processing step that results in a complex but monolithic high performance 3D vector field device. We fabricated devices with equivalent sensitivities in all directions, angular accuracy of 0.14° , as well as low noise and low power consumption during high-speed operation at frequencies up to 1 kHz. Contributed talk, Thu./19:20

Ultrafast temperature measurements for laser applications

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One of the fundamental issues in light-matter interaction is the evaluation of the target temperature. Most often, the temperature of the irradiated object is determined by the energy balance equations. In the case of slow stationary processes, these calculations can be verified by direct temperature measurement performed with a pyrometer, thermocouple or thermistors. The response time of such detectors is limited by their thermal capacity and the time required to transfer heat from the tested object to the detector. In the case of pyrometers, time constraints are also bound by optical chopper modulation frequency (usually from approximately 1 to 10 kHz). These limitations make impossible to carry out a direct temperature measurement when we are working with a pulsed laser and its 10ns-long single pulse duration. Such lasers are often used for heating, welding, cutting, ablation of materials and direct laser interference lithography $(DLIP)^{(1)}$. High power pulses will also alter material optical properties during the thermal processing (heating/cooling). The temperature change the absorbed energy part in time which is difficult to include in the theoretical models. In this study we demonstrate the results of direct temperature measurement carried out at thin Bi(40nm)/Cu(40nm) metallic bilayer deposited on a polymer substrate. The thermoelectric effect at the Bi/Cu interface allows us to probe temperature with temporal resolution up to 1ns. The developed method allows us to determine the temperature of the ablation threshold and the direct heat accumulation processes in the material irradiated by a series of pulses. This work presents the results of measurements, accompanied by the finite element method (FEM) calculations. Further work is in progress to develop the flexible sensor platform for ultrafast temperature measurements and its applications.

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Contributed talk, Thu./19:40

Thin conducting MoO_3 films on copper for technological applications

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The researches on thin films of transition metal oxides have triggered an enormous interest in applications but also in the understanding of novel phenomena, both for technological applications and fundamental science perspectives ⁽¹⁾. In this research, we focused on a particular transition metal (TM) oxide, the molybdenum (VI) oxide (MoO3) deposed on Cu substrates. MoO3 is an insulating oxide and also a natural layered van der Walls material. When deposited as a thin layer (e.g., 300 nm) on copper it exhibits unique properties ⁽¹⁻³⁾. Actually, these thin layers of molybdenum trioxide deposited on copper tends to be conductive, while the work function remains almost constant and higher than that of the copper surface ⁽⁴⁻⁶⁾.

Here we will present the development and the optimization of the vapor deposition process and the characterization of the physical and chemical properties of the deposited films. By using Raman spectroscopy, Auger electron spectroscopy and X-ray absorption spectroscopy, we also characterized the structural order and the electronic properties of these films. In particular the XANES spectroscopy probed the presence of insulating or metallic oxide phases and correlate the electronic properties with the conductivity properties of these coatings $^{(5,6)}$. To improve the adhesion properties of the film, an annealing procedure was developed, with different thermal treatments. With scanning electron microscopy, X-ray absorption and Raman spectroscopies, we were able to demonstrate that the optimized procedure allows ordering of the film, minimizing the reduction of molybdenum atoms and the oxidation of the copper substrate $^{(5)}$.

Due to its unique properties, MoO3 is an interesting material for protecting the surface of accelerating RF cavities. Due to the low WF, the performance and the lifetime of a copper RF cavity are affected by breakdown phenomena⁽⁶⁾. A high work function conductive coating could be used to reduce these damaging phenomena, extending the lifetime of the device and allowing it to operate at higher electric fields^(2,5,7,8). For this reason we also tested MoO3 thin films deposed on copper exposing the surface to high intensity THz pulsed radiation at different incidence angles. In spite of the low thickness (100-200 nm) these coatings significantly reduce the damage of the copper surface⁽⁵⁾.

Part of this work has been performed in the framework of DEMETRA, a project funded by the INFN Vth Committee and with the support of the Bilateral Cooperation Agreement between Italy and Japan of the Italian Ministry of Foreign Affairs and of the International Cooperation (MAECI) in the framework of the project of major relevance N. PGR00728.

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Contributed talk, Thu./20:00

Ex situ measurements of titanium thermal oxidation at PEEM/XAS beamline at SOLARIS

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Thanks to photoinduced properties and a huge number of applications, especially in the chemical industry, titanium dioxide is the most studied titanium compound in the world. TiO₂ future applications are focused on such areas as renewable energy, environmental protection and medicine⁽¹⁾. The mechanical properties and biocompatibility of titanium have influenced its widespread use in implantology. In many works, it has been shown that the titanium dioxide layer on titanium implants can protect implants against corrosion and promote cell adhesion⁽²⁻⁴⁾. Since the naturally occurring layer of passive oxide on titanium implants is too thin to provide sustained wear resistance, the thermal oxidation of titanium becomes a simple and economical solution^(4,5). Thermal oxidation not only increases the thickness of the oxide layer but also promotes the formation of the rutile phase, which is characterised by excellent adhesion to the titanium substrate, low friction and excellent wear resistance⁽⁶⁾.

In the presented work, we have shown changes in the electronic structure and kinetics of phase transformations (metal – anatase – rutile) during thermal oxidation of titanium metal discs. The process was followed by ex situ measurements using X-ray Absorption Spectroscopy method at PEEM/XAS beamline at SOLARIS. The XAS detection was performed in the total electron yield (TEY) mode, which gave information about surface states of titanium discs oxidized at different temperatures (25°C-800°C). Kinetics of the metal - anatase - rutile transformation is determined from the XAS spectra measured at different oxidation temperatures.

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Contributed talk, Thu./20:20

Polish Free Electron Laser-Scientific Case

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PolFEL-the Free Electron Laser in Poland, located at the area of NCBJ (30 km from Warsaw Centre) is a project to deliver photon output in the range from THz to VUV (including IR) based on a combination of advanced conventional lasers and an accelerator continuously delivering electron bunches from a superconducting photocathode. This is a 4th generation light source. THz and IR radiation is generated in periodic magnetic undulator supperradiant type, while VUV in undulator based on the self-organized "microbunching". PolFEL will provide electron bunch with duration of about 10 picosecond and ultra-short femtosecond photon pulses. The time duration adjustment is possible on user demands. Photons parameters will be monitored during run time with diagnostic systems. The experimental setup will allow for studies of physical and chemical properties of solid states, gases, and liquid samples. Moreover, the experimental stations are designed in cooperation with experimental groups from Institute of Biochemistry and Biophysics Polish Academy of Sciences and Military University of Technology.

Invited talk, Fri./08:30

Tapping-AFM-IR: a versatile tool to characterize polymeric nanoparticles

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Since 10 years, a new instrumentation, called AFM-IR, has been developed in our team at the Chemical-Physics laboratory (LCP, Université Paris-sud) to perform IR spectromicroscopy analyses at the nanoscale. This technique is based on photothermal effect⁽¹⁻³⁾ and is the result of a coupling between atomic force microscopy (AFM) and IR spectroscopy to perform local IR absorption measurements (Patent US11 / 803421, A. Dazzi). This combination makes it possible to identify at the nanoscale organic molecules without using exogenous markers. The application fields range from biomedical, to polymer science and astrochemistry.

In our team, the technique has shown its potential in the study of lipid bodies in microorganisms. Nevertheless, in its initial configuration, the instrumentation has reached a limit in term of sensitivity: the size of the smallest object (chemically pur) detectable is around 50 nm. New experimental approaches are therefore developed to solve the problems and overcome the technical constraints imposed by the system itself (configuration of illumination - sensitivity -study of soft sample...).

In particular, two changes were significant:

First, a change of configuration was done that allowed us to go down in terms of resolution and to reach tens of nanometer. This breakthrough offers new perspectives such as the study of protein fibers or nanoparticles. The second concerned the AFM imaging itself: AFM-IR was used mainly in the contact mode, thus preventing its application in soft or loosely adhered samples such as polymeric nanoparticles (NPs) of less than 200 nm. Here, we will present an application of tapping AFM-IR, which enabled addressing the limitations of the contact mode AFM, thus extending its application to unraveling the chemical and morphological features of soft, spherical samples difficult to fix on the AFM substrate ⁽⁴⁾.

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Invited talk, Fri./09:00

Nanoscale X-ray imaging and spectroscopy at third generation synchrotron sources

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X-ray Fluorescence (XRF) is a rapidly evolving analytical technique which allows visualizing the trace level metal distributions within a specimen in an essentially non-destructive manner. The different length scales to which XRF imaging can be applied includes, among others: sub-mm resolution imaging of whole animal sections, micro-imaging of millimetre-sized model organisms and finally nanochemical imaging of single cells. In this presentation, the basic principles of X-ray fluorescence imaging and analysis at third generation synchrotron sources will be explained. Different scanning geometries among which two-dimensional (2D), computed tomography (CT), confocal and full-field XRF imaging will be illustrated. XRF analysis of biological samples pose a significant challenge as they need to be converted from their aqueous state to a chemically representative state also stable during irradiation, using sample preparation methods such as resin-embedding, freeze-drying or ideally, vitrification. The pros and cons of these methods will be discussed and the sample preparation workflow to go from live cell culture to cryofrozen cells will be detailed.

At third generation synchrotron radiation (SR) sources, detection limits at the sub-ppm level can be obtained with spatial resolution of 50 nanometer (nm) and below, reaching the single atom detection level. These offer fascinating capabilities for nanochemical imaging of metals within single cells. Complementary techniques such as three-dimensional X-ray phase contrast imaging provide nanoscopic morphological information, enabling element-to-organelle correlation. Practical examples of nanochemical imaging upon cryofrozen tissues and cells at three state-of-the-art facilities will be provided: 1) the 9-ID Bionanoprobe at the Argonne Photon Source (APS) in Argonne, USA 2) the P06 Hard X-ray Micro/Nanoprobe at the PETRAIII synchrotron in Hamburg, Germany and 3) the ID16A 'nano-imaging' beamline at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France.the ID16A 'nano-imaging' beamline at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France.

Invited talk, Fri./09:30

X-ray spectroscopy of magnetic nanoparticles in solution

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Quantitative determination of magnetic properties of nanoparticles in solution is a tricky task. Results obtained by volume magnetometry, e.g. VSM or SQUID, are prone to systematic errors due to uncertainty in concentration, size distribution and chemical composition of particles. Recent advances in probing magnetic properties of nanoparticles in solution using hard X-ray photonin photon-out magnetic spectroscopy will be shown. Details of the experimental procedure will be illustrated by the results of measurements performed on liquid and frozen dispersions of particles. The feasibility of probing carrier-free element and site selective magnetization profiles of ferromagnetic and superparamagnetic nanoparticles in solution will be discussed.

Invited talk, Fri./10:00

Towards structure activity relationships governing nanoparticle toxicology

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Engineered nanomaterials are increasingly being developed for paints, sunscreens, cosmetics, industrial lubricants, tyres, semiconductor devices, and also for biomedical applications such as in diagnostics, therapeutics, and contrast agents. As a result, nanomaterials are being manufactured, transported, and used in larger and larger quantities, and potential impacts on environmental and human health have been raised. Polymeric dendrimers, both poly(amidoamine) (PAMAM) and Poly(propylene imine) (PPI), are specifically suitable for biomedical applications. They are well-defined nanoscale molecules which contain a 2, or 4, -carbon core and primary amine groups at the surface, the number of which precisely doubles with each increasing generation. The systematically variable structural architecture and the large internal free volume make these dendrimers an attractive option for drug delivery and other biomedical applications.



Structure of closely related dendrimer series (A) Poly(amido amine) (PAMAM), (B) Poly (propylene imine) (PPI).

In addition to the fact that the Organisation for Economic Co-Operation and Development (OECD) have included them in their list of nanoparticles which require toxicological assessment, the systematically variable physico chemical structures make them ideal for exploring quantitative relationships which govern their cellular uptake, interactions and biological responses. The presentation will review the studies of the generation and dose dependent uptake and response mechanisms, and pointers towards the establishment of predictive toxicological methods. Numerical simulations are employed to support the approach. Invited talk, Fri./11:00

Shapeable magnetoelectronics

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Electronic devices are continually evolving to offer improved performance, smaller sizes, lower weight, and reduced costs, often requiring state of the art manufacturing and materials to do so. An emerging class of materials and fabrication techniques, inspired by self-assembling biological systems shows promise as an alternative to the more traditional methods that are currently used in the microelectronics industry⁽¹⁾. Mimicking unique features of natural systems, namely flexibility and shapeability, the geometry of initially planar microelectronic structures can be tailored leading to thin and ultrathin flexible, stretchable and printable magnetoelectronics (1-6). The small thickness of the polymeric substrates of less than 1 μ m prevents the electronics from degradation upon severe mechanical deformations, e.g. bending to the curvature radii of about 10 micrometers. Involving self-assembly strategies realization of spatially non-trivial electronic and magnetoelectronic devices in a compact form and with a reduced number of fabrication steps become feasible with novel shapeable ultrathin hydrogel based polymeric substrates⁽¹⁾. The swelling state of the hydrogel can be affected by tailoring the environmental conditions, including temperature, solution composition and pH providing full control over the shape of the device. The opportunity to reshape the device on demand is appealing for the implant applications allowing a soft attachment to the gentle biological tissue⁽⁷⁾. Furthermore self-reshaping electronics enabled new easier opportunities in fabrication of electromagnetic devices such as microwave helical antennas, coils and magnetic sensors with non-planar cylindrical geometry, which manufacturing is rather challenging when conventional fabrication techniques are applied (1,8-10).

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Invited talk, Fri./11:30

Magnetism and Synchrotron Radiation

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Magnetism has been known to mankind for more than two thousand years. Its first notable technological application has probably been the compass, which still proofs itself as an invaluable tool.

In the meantime magnetism has become ubiquitous in our daily live. The prototypical horse-shoes magnet has evolved to generate different families of magnetic devices like electro-magnets, superconductive magnets, or more complex structure like composite magnetic materials used to store data in computers.

On the other hand, since their discovery, x-rays have proven as a fundamental tool to investigate solid-state physics. With the advent of synchrotron radiation intense and collimated x-ray beams are routinely available to scientist studying not only physics, but also chemistry and biology. How- ever, due to their electromagnetic nature, x-rays are well suited to study also magnetic materials. In this talk I will give an overview of some of the possibilities offered by synchrotron x-ray radiation to study magnetic properties in solid-state physics using techniques as X-ray Magnetic Circular Dichroism (XMCD), X-ray Magnetic Diffraction (XMD) and recent development in imaging of magnetic moment configurations in bulk samples.

Invited talk, Fri./12:00

Analytical approaches for Helium Ion Microscopy

G. Hlavacek

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Helium Ion Microscopy (HIM) utilizes a Gas Field Ion Source (GFIS) to create a Helium or Neon ion beam with a diameter better than 0.5 nm and 1.8 nm, respectively. The method is well known for its high resolution imaging and nanofabrication capabilities which it is able to provide not only for conducting but also insulating samples without the need for a conductive coating. However, the existing GFIS based focused ion beam (FIB) tools suffer from the lack of a well integrated analytic method that can enrich the highly detailed morphological images with material properties contrast. While HIM technology is relatively young several efforts have been made to add such an analytic capability to the technique. So far, ionoluminescence, secondary electron spectroscopy, backscattering spectrometry (BS), and secondary ion mass spectrometry (SIMS) using a magnetic sector or time of flight (TOF) setup have been demonstrated. In addition, in-situ experiments can be performed that allow to directly and in real time investigate the effect of the focused ion beam on the materials under various conditions.

I will present our efforts to perform in-situ experiments in the Helium Ion Microscope and enhance its analytic capabilities. In the first part of my presentation I will give an overview of the in-situ characterization capabilities of the Orion NanoFab including in-situ heating and electrical characterization. In the second part of the talk I will focus on different analytic approaches tested so far. I will briefly give an overview on ionoluminescence in the HIM and than present our newly developed TOF-BS and TOF-SIMS setup which allow to obtain information on the composition of the sample. They both utilize the same cost efficient and minimal invasive pulsing scheme for the primary ion beam. The lateral resolution reached for TOF-BS is approximately 50 nm while for TOF-SIMS a value of 8 nm could be reached. First images will be presented and the performance of the TOF-SIMS spectrometer will be discussed. Hamamatsu, Fri./12:30

Guest talk from Hamamatsu Photonics Deutschland GMBH

<u>J. Baszak</u>

Hamamatsu Photonics Deutschland GMBH, Arzbergerstr. 10, 82211 Herrsching a. Ammersee, Deutschland Contributed talk, Fri./14:00

Stimulation of the antitumor response by simultaneous administration of low doses of MAPK pathway inhibitor and mGluR1 antagonist in melanoma

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Introduction: The main cause of melanoma is the BRAF kinase mutation. Currently used new generation drug is an inhibitor of this kinase, which successfully inhibits the growth of cancer cells. On the other hand, its activity leads to significant toxicity of normal cells, which results in many serious undesirable effects. The aim of the study is the use a combined therapy based on the simultaneous administration of two inhibitors of the MAPK pathway at low doses, which can reduce the adverse effects, while maintaining the therapeutic effect.

Results: For the analysis were taken four biomarkers participated in the tumor process, respectively: Bcl-2, EGF, MDM2 and COX-2 which determine cell proliferation. The pro- and antiapoptotic genes expression was investigated by Real-time PCR method. The cytotoxicity of the tested compounds and activity of cells was measured by MTT test. Our study showed that simultaneous administration of mGluR1 antagonist and BRAF kinase inhibitor significantly decreased the proliferation factors and survival of cancer cells. Moreover, due to the low doses of used compounds, there was no significant effects on normal cells metabolism.

Conclusions: Currently used chemotherapy is associated with toxicity due to the high doses of drugs. Therefore, we postulate to decrease the side effects by using the combined pharmacotherapy in low doses. Summarizing, conducted studies on melanoma model and using two compounds, involving affinity to mGlu1 receptor and BRAF kinase, may be an alternative and effective way to reduce the side effects, while maintaining the antineoplastic effect. Contributed talk, Fri./14:20

Influence of therapeutic proton beam on glioblastoma multiforme proliferation index – preliminary study

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Glioblastoma multiforme (GBM) is one of the most common and aggressive type of primary brain tumour mostly due to being resistant to current chemo- and radiotherapies.

The aim of this study was to investigate the influence of the rapeutic proton beam or X-rays on proliferation of U251 MG and U118 MG glioblastoma cell lines (WHO grade IV). U251 MG and U118 MG cell lines were cultured and further irradiated with 0.5 Gy to 10 Gy of either proton beam (70 MeV) or X-rays (250 kV). After 72 hours of culture cytokinesis-block micronucleus (CBMN) as says were carried out to study changes of proliferation presented as nuclear division index NDI.

Also, the integrity and quantity of RNA (RIN, RNA Integrity Number) were studied by the Agilent 4200 TapeStation System and a Tecan Spark microplate reader.

Preliminary results suggest that both protons and X-rays influence GBM cellular proliferation and RNA integrity to different degrees. Generally, therapeutic proton beam was more effective in inhibition of proliferation than X-rays, what was better seen for U251 MG cell line. Therapeutically valuable statistical differences in NDI values between U251 MG and U118 MG cell lines were only found after X-rays in the whole dose range (p<0.05). The NDI decreasing (R2 = 0.819) was only found for U251 MG cell line with an increasing in the proton dose. These cells can be classified as more radiosensitive than U118 MG cell line due to genetic differences between cell lines, what is planned to be studied by gene expression analysis. Acknowledgments: This study was partially funded by the Horizon 2020 UE project entitled "INfraStructure in Proton International REsearch", INSPIRE, No. 730983; National Science Centre, Poland Grant No. DEC-2013/09/D/NZ7/00324 (access to laboratory equipment) and MNiSW 7150/E-338/M/2014. The research was partially performed at the Institute of Nuclear Physics Polish Academy of Sciences using the equipment purchased in the frame of the project co-funded by the Malopolska Regional Operational Program Measure 5.1 Krakow Metropolitan Area as an important hub of the European Research Area for 2007–2013, project No. MRPO.05.01.00-12-013/15.

Contributed talk, Fri./14:40

Raman analysis of biological materials supported by chemometrics

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Raman spectroscopy is widely applied for biochemical analysis of tissues. cells, and cell organelles. It provides detailed molecular information about the sample and can easily detect structural changes at the micro- and nano-scale levels. Furthermore, as an optical technique it is non-invasive and non-destructive. It allows the analysis of cells or tissues without perturbation of the sample. Moreover, Raman spectroscopy is label free, and has the advantage over other microscopic techniques that it can simultaneously detect a variety of molecular structures, such as proteins, nucleic acids (DNA and RNA), and lipids, in a single acquisition. However, most differences between Raman spectra of biological materials caused by exogenous factors are subtle. Thus, detailed analysis of variations in Raman spectra induced by these factors is challenging and requires application of advanced multivariate statistical methods. The most popular chemometric methods in spectroscopic analyses are Principal Component Analysis (PCA), Partial Least Squares Regression (PLSR), and Cluster Analysis (CA). These methods streamline analysis of large spectroscopic datasets and support identification of those factors which have a minor effect on the spectra. In our study, we applied selected chemometric methods (PCA, PLSR, CA) for detailed analysis of Raman spectra collected from prostate cancer cells treated with ionizing radiation and from urinary extracellular vesicles of diabetic patients. The chemometric methods allowed to identify the effect of X-ray irradiation on the individual cell organelles (nucleus, cytoplasm, lipid droplets) as well as to find potential biomarkers responsible for diabetes disorder in humans.

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Contributed talk, Fri./15:00

Development of laboratory X-Ray spectroscopy methods for biological applications

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Nowadays the number of cancer diseases is drastically increasing and going to be higher in the next years. The new anticancer drugs are being studied to prevent from obtaining side-effects and chemoresistance, which commonly used platinumbased chemotherapeutics cause. To obtain anti-tumor drugs with demanded properties, non-platinum metal compounds are being explored.

In this study, copper based complex with 1,10-Phenanantroline is being investigated for determination of electronic structure around metal center. The laboratory wavelength-dispersive X-ray methodology has been developed to perform X-ray absorption spectroscopy (XAS) measurements. This approach allows for low-costs and accessibility of measurements that usually are performed on synchrotron radiation sources. It enables studies of sample structure at atomic and molecular level, as well as its chemical properties. We will present methodological approach to laboratory XAS measurements and examples of experimental K-edge copper XAS spectra of various Cu compounds.

Thanks to the proposed developments, it will be possible to do the measurements in the conditions mimicking physiological ones. It will also enable to investigate cytotoxicity of the used copper compound with measurements of its interactions with DNA, what will be the next step of the research.

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Contributed talk, Fri./15:20

Using wide-angle X-ray diffraction to understand the structure of complex materials used in pharmacy and medicine

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Nowadays, the use of complex pharmaceutical or medical formulations is highly desirable to overcome barriers such as low bioavailability and insufficient solubility. Such formulations include amorphous or disordered phases, nanoparticles, composites, and mixtures with molecular or polymeric excipients. Such complex materials can not typically be structurally characterized by the methods used for crystals. Conventional X-ray or neutron diffraction loses its power when the crystallite size becomes nanometer in scale. Moreover, challenges are raised when applying standard diffraction technique to materials with disorder and imperfections. To truly harness the power of such materials, we must understand the relationship between atomic structure and macroscopic properties. However, the atomic structure of highly complex materials can be extremely difficult to solve. Therefore, new analytical methods must be utilized to better understand these materials.

Recently, the development of the wide-angle X-ray diffraction and total scattering pair distribution function has shown great promise for fingerprinting, quantification and modelling of complex materials. Total scattering, collected in the wide-angle X-ray diffraction experiment, utilises not only Bragg scattering from a material but also the diffuse scattering in order to look beyond the average structure to examine the local, or short-range structure. The pair distribution function is a representation of the diffraction data in real space. As such it not only represents a good fingerprint of a material structure, but it is also a very intuitive function, allowing rapid investigation of structures, and changes in structure. Most importantly in the context of on-crystalline materials, unlike crystallography, it does not assume a long-range ordered crystalline structure. It may still be used for clumps of packed molecules as small as few nm, indeed for studying the molecule itself.

In this work some examples of using wide-angle X-ray diffraction to understand the atomic structure of materials used in pharmacy and medicine will be presented. Contributed talk, Fri./15:40

Scintillating hafnium dioxide based materials with potential in medical imaging

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X-rays excited luminescence materials get more important in modern biology and medicine. One important reason for that is application of X-rays in photodynamic therapy (PDT) and therefore treatment of cancer. Requirements for such materials are high mass attenuation coefficient and intertness in biological processes. Promising material for this application is hafnium dioxide, which exhibits high density and compatibility with living organisms, which was tested both in the short and long timespan. To show well established luminescence, not depending on the surroundings, lanthanide ions are used as activator. In this work we show synthesis of Eu_{3+} doped HfO₂ nanoparticles with use of microwave hydrothermal technique. As the sensitizers, ions with s² electronic configuration were used. Structural and spectroscopic properties of obtained nanoparticles are revealed. Also, various modalities of the material were shown in medical imaging as well as potential in therapy and diagnosis.

Contributed talk, Fri./16:30

XUV coherence tomography with nanoscale resolution driven by broadband XUV sources

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Optical coherence tomography (OCT) is a well-established method to retrieve three-dimensional, cross-sectional images of biological samples in a non-invasive way using near-infrared radiation. The axial resolution of OCT is on the order of the coherence length $l_c \propto \lambda_0/\Delta\lambda$ which depends on the central wavelength and the spectral width $\Delta\lambda$ of the light source. As a consequence, the axial resolution only depends on the spectrum rather than the geometrical properties of the radiation. OCT with broadband visible and near-infrared sources typically reaches axial (depth) resolutions on the order of a few micrometers. Since its invention in the early 1990s by Huang et al.⁽¹⁾, OCT has become a well-established and standard diagnostic method in medicine especially for investigating the retina in vivo⁽²⁾.

In this contribution, we present the extreme ultraviolet (XUV) coherence tomography (XCT) $^{(3-5)}$, utilizing short coherence length of broadband XUV and so X-ray (SXR) radiation delivered by synchrotron and table-top sources. Powerful capabilities of XCT can be demonstrated when employed for investigation of samples in their native spectral transmission windows. For instance, in the silicon transmission window (30-99 eV) a coherence length of about 12 nm hold promise for application of XCT in the growing sector of semiconductor metrology. In the water window (280-530 eV), in turn, the coherence length as short as 3 nm paves the road towards applications in life sciences.

In the experiment, we investigate a sample consisting of two laterally structured gold layers of nanometer thickness buried in a silicon matrix. Reconstructed 3D PR-XCT measurement reveals detailed 3D information on the sample. e demonstrated axial resolution is 24 nm. Remarkably, the XCT reveals a high material sensitivity by resolving a thin Silicon dioxide layer (blue) localized at depth of about 160 nm has been detected. is nanometer-thin layer has been developed dur- ing the production process of the sample. Such contamination remains elusive for the SEM and remains barely visible in the TEM image. The XCT tomograms are analyzed by the phase-retrieval algorithm capable of extracting material information buried inside of the sample.

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Contributed talk, Fri./16:50

Dynamic hydration function of human serum albumin adsorbed at silicon oxide surface

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A controlled adsorption of biomolecules at various surfaces enables efficient protein separation for biosensing and bioreactors. Although the subject has been extensively studied, mechanisms of protein adsorption still require fundamental explanation^(1,2). Discrepancies in the interpretation of experimental data still appear in respect to basic aspects such as: the driving forces, monolayer structure and stability, reversibility of adsorption, degree of conformational changes, interpretation of isotherms and maximum coverage⁽³⁾.

In this work, attention is focused on human serum albumin (HSA- most abundant serum protein) in an attempt to reveal protein adsorption mechanisms. Adsorption kinetics of HSA at silica substrates was studied using the QCM-D, OWLS and AFM methods as a function of ionic strength at pH 3.5. The obtained experimental data were calibrated using the dry coverage of HSA derived from AFM imaging and from the mass transfer equation solution. Thus, the dynamic hydration functions and water factors of HSA monolayers were quantitatively evaluated. The HSA adsorption runs were converted to the dry coverage vs. the time relationships, using the hydration function. It allowed to determine the maximum coverage of irreversibly bound HSA molecules. The parameter was equal to 0.4 and 1.4 mg m-2 at pH 3.5 and for NaCl concentration of 0.001 and 0.15 M. respectively. These results confirm previous experimental data for mica derived by streaming potential measurements combined with theoretical modelling $^{(4)}$. In this way, the side-on mechanism of HSA adsorption at silica sensor at pH 3.5 was confirmed. In addition, a quantitative analysis of the HSA desorption runs allowed to calculate the binding energy of reversibly adsorbed HSA molecules. Therefore, these results enable to develop a robust technique of preparing HSA monolayers at silica sensor of well-controlled coverage and molecule orientation.

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Contributed talk, Fri./17:10

How Cr(VI) reduction affects lipid membrane structure?

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Chromium-VI (Cr(VI)) is a toxic and highly carcinogenic agent, which is increasingly released into environment. This poses an enhanced risk of cancer and other Cr(VI)-related diseases development in population⁽¹⁾. At a cellular level, Cr(VI) poisoning starts from interaction between Cr(VI) factor and cellular membrane surface. Then, Cr(VI) rapidly starts to oxidise membrane components, reducing itself throughout Cr(V) and Cr(IV) species, up to Cr(III)⁽²⁾. Except extensive damage to cell surface, creation of radical Cr(V), enables Cr to bind to membrane molecules directly. Additionally, Cr(VI) has high permeability rate throughout lipid membranes via anionic exchange mechanism^(3,4), although channels included in such process could be eventually destroyed due to Cr(VI) high oxidation potential.

In presented study, liposomes were used as a model of cellular membrane, because they mimic its properties and have simple composition.1,2-dimyristoylsn-glycero-3-phosphocholine (DMPC) and DMPC:DOPE (DOPE - 1,2-dioleoyl-snglycero-3-phosphoethanolamine) liposomes were treated with $K_2Cr_2O_7$ as source of Cr(VI) oxidizing agent. Using combined X-Ray Absorption Spectroscopy, X-Ray Fluorescence and X-Ray Diffraction approach we have obtained an evidence, that Cr content was tightly bonded to the cellular membrane in form of Cr(IV) state. Amount of bonded Cr was slightly growing along with increasing content of DOPE in liposomal mixtures and Cr(VI)/Cr(IV) ratio was significantly decreased for more fluid liposomes. Moreover, XRD experiment has evidenced that Cr(VI) membrane internal order decreased in less fluid membranes. On the other hand, it was only slightly changed in more fluid ones. Additionally, it was observed that global liposomal size changed. Based on literature data and our results, we have proposed a model of Cr interaction with model lipid membrane in which, due to lipid oxidation, hydrophilic channels are created. This model comprises all known membrane properties along with good agreement with experimental results. Our results are step forward into understanding of Cr(VI) poisoning etiology. In future, they may help to develop a way to prevent Cr poisoning and methods of effective treatment in such cases.

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Contributed talk, Fri./17:30

From macroscopic studies to microscopic properties: unravelling the conformation and adsorption mechanisms of poly-L-lysine at solid/liquid interfaces

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Efficient adsorption of macrocations onto solid surfaces determine is a prerequisite for the broad range of their applications. Poly-L-lysine (PLL), whose molecule is composed of naturally occurring lysine amino acid residues, has acquired considerable attention for many practical applications such as controlled drug delivery, immunosensing, protein immobilization and separation. However, despite the extensive experimental effort, the fundamental physicochemical properties of PLL molecules in aqueous solutions remain largely unknown. To fill up this gap, thorough physicochemical characteristics of PLL in electrolyte solutions and at solid/liquid interfaces were performed, using complementary experimental techniques such as micro-electrophoresis (LDV), dynamic light scattering (DLS), dynamic viscosity, and streaming potential. It is worth underlying that the role of pH has been systematically evaluated in these measurements, especially the effective electrokinetic charge of PLL monolayer under various conditions was evaluated. Moreover, using these techniques and the molecular dynamics modeling, such parameters as the molecule density $(1.6 \times 10^3 kq/m^3)$, the chain diameter (0.92 nm), the monomer length (0.33 nm), and the cross-section area in the side-on orientation depending on ionic strength were determined for the first time. Knowing these parameters, the PLL adsorption kinetics on mica was derived from the random sequential adsorption (RSA) and the streaming potential method. The experimental data were successfully interpreted in terms of the theoretical results derived from the 3D electrokinetic modeling, which confirmed the side-on adsorption of PLL moleceules on the surface with the fraction of side-on with crossing adsorption for the coverage above 0.3. Additionally, using this method, the stability of the monolayers, evaluated via desorption kinetic measurements, was determined. It was shown that PLL molecules adsorbed in the side-on conformation remain irreversibly bound with the surface. Our studies proved that it is feasible to obtain stable PLL monolayers of controlled density and structure, which can be used as supporting layers for nanoparticle and protein immobilization or in the layer-bylayer processes for microencapsulation.

Poster No. 1

Spectral emission measurements from laser-produced plasma SXR-EUV source based on a double stream gas puff targets

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X-ray technology has seen tremendous development since its discovery by W. Röntgen in 1895. Main sources which were prominent in the field were X-ray tubes, synchrotrons, undulators, and X-ray lasers. X-ray research has gained significant importance in the field of astrophysics, medicine, and atomic physics. X-ray spectroscopy has provided huge contributions to the explanations of the atomic structure of elements. Extreme-ultraviolet (EUV) and soft X-ray (SXR) radiation sources have gained significant attention in recent years^(1,2). The main sources which are used for generation of SXR EUV rays are synchrotrons, high order harmonics generation (HHG) sources and laser-produced plasmas⁽³⁾. Laser plasma X-ray sources based on double gas puff targets are very compact, efficient and convenient for many applications including X-ray microscopy and optical coherence tomography^(4,5). Detailed characterization of such sources based on different gas targets are very important in terms of a wide range of applications being developed in SXR EUV range of EM spectrum.

We present a detailed spectroscopic study of this source in the wavelength range from 1 nm to 70 nm by combining the spectral data from three different spectrometers: SXR grazing incidence spectrometer (GIS) in the range of 1 to 5 nm wavelength, transmission grating spectrometer in a range of 4-14 nm and finally the EUV GIS spectrometer registering spectral information from 10-70 nm wavelength. The measurements show possible candidates for a gas target for laserplasma source dedicated to both EUV and SXR spectral ranges. We have evaluated eleven different gases as gas puff target in which laser plasma is generated using a 1064 nm Nd: YAG laser pulses of duration 4 ns and with an energy of 737 mJ. We could identify different characteristic atomic transition of several elements in the range 1nm-70nm of the spectrum. In the proposed presentation we detail the experimental setup and results obtained from our spectral investigation on eleven gases which are convenient to be used as gas puff target for laser plasma X-ray sources. We also identify the specific applications for which the particular gas targets can be used after evaluating their spectra.
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Magnetoresistive properties of iron oxide nanoparticles arrays in conducting matrix

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Important parameters for the characterization of nanostructures are the peculiarities of packaging, the distance between the nanoparticles (NP), the number of monolayers, the cluster nature of the coatings and the annealing temperature (see, for example,⁽¹⁾). As application methods, the modified Langmuir – Blodgett (LB) technique and the method of spin coating were used. Conductive matrix of non-magnetic material (Ag) was deposited by thermal evaporation in vacuum 10-4 Pa, both before and after the temperature treatment ordered NP arrays.

To minimize the diffusion processes between nanoparticles and a conductive matrix, a temperature processing of arrays of NP was carried out prior to application of a conducting matrix. In the case of $(Ag+NiFe_2O_4)$ NP, annealing at a temperature of 1100 K leads to the formation of several phases (Fe, Ni, FeNi₃), while the Fe₃O₄ nanoparticles are converted into Fe nanoparticles. It is established that after high temperature annealing at 1100 K, the formation of traces of oxides γ -Fe₂O₃ is observed, indicating the formation of a thin oxide shell on the surface of single-phase particles. Directly heat treatment leads to the NP coalescence, which involves an increase in the amount of magnetic material in a single particle and, as a consequence, an increase in their magnetic moment.

It was found that annealing at 600 K leads to an increase of the value of MR for $(Ag+CoFe_2O_4)$ structures up to 13% and $(Ag+Fe_3O_4)$ to 6%. The influence of the thickness of the conducting non-magnetic matrix of Ag and its temperature processing on the magnetoresistive properties of iron oxide nanoparticles arrays has been analyzed and it has been established that annealing leads to an increase in the MR magnitude from 3 to 20%. The largest MR magnitude are observed at a thickness conducting matrix 5 nm, which is explained by the increase in the number of interfaces for spin-dependent scattering of electrons.

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Characterization of glioblastoma mechanical properties using atomic force microscopy

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Glioblastoma is one of the most dangerous cancers of the central nervous system occurring with a frequency of 5.8 and 4.1 per 100,000 people respectively for men and women in developed countries. Due to its invasiveness within brain structures and rapid growth it was placed in the WHO classifications as a fourth grade cancer. Despite continuous progress in diagnosis and treatment methods, the prognosis are poor and the average survival time is only a dozen months. Therefore, better understanding of the mechanopathology of these cancers, might open a new window for developing more efficient treatment options.

In this study, the atomic force microscope (NanoWizard 4 BioScience, JPK Instruments) working in the force spectroscopy mode was used to assess the viscoelastic properties of white matter, gray matter and cancerous tissues. Probes with spherical geometry ($\emptyset = 4.5 \ \mu m$) were used to register force-distance curves. The analysis of these curves was based on the Hertz model, and the determined values of the Young's modulus have been presented in the form of distributions. The obtained results show a several-fold increase in the stiffness of grade IV glial tumors compared to the gray matter, while margin samples were relatively close to the grey matter. At the same time, stiffness distributions of cancerous tissues are highly heterogeneous, that confirms the inhomogeneity of the probed cancer samples.

Strain-induced perpendicular magnetic anisotropy and Gilbert damping in $Tm_3Fe_5O_{12}$ thin films

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In the attempt of implementing iron garnets with perpendicular magnetic anisotropy (PMA) in spintronics, the attention turned towards strain-grown iron garnets. One candidate is $Tm_3Fe_5O_{12}$ (TmIG) which shows strain-induced PMA when grown under tensile strain. Possible substrate choices are GGG(111) and substituted-GGG(111) substrates, where the latter generated a higher in-plane tensile strain for the growth of TmIG. TmIG films with thicknesses between 20 and 300 nm were grown by PLD on sGGG(111) substrates. XRD measurements showed that films thinner than 200 nm exhibit in-plane tensile strain, thus, they meet the requirement for PMA. As expected, these films show PMA due to strain-induced magneto-elastic anisotropy. However, with increasing film thickness a relaxation of the unit cell towards its bulk structure is observed resulting in a rotation of the magnetic easy axis from out of the sample plane towards the sample plane. The Gilbert damping parameter extracted from FMR measurements is in the range of 0.03 independent of the film thickness.

Modelling of the X-ray emission spectra of DNA damaged by UV radiation

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Radiation interaction with matter and its effects on living cells are crucial in aspect of radio- and phototherapy. DNA molecule is especially relevant, because DNA lesions affect on all cell functions. Solar UV radiation has strong impact on human skin damage, despite the fact that 99% percent of it has only heating properties⁽¹⁾. UV induced DNA lesions are the main external factor causing melanoma, which incidence rate is the most rapidly increasing among all cancers over last thirty years in Poland⁽²⁾. Annually there are 3100 cases diagnosed in Poland⁽²⁾, 15 906 in UK⁽³⁾ and 96 408 in USA⁽⁴⁾.

DNA backbone lesions, induced by UVB radiation, are mainly pyrimidine dimers produced due to breaking hydrogen bonds between nitrogen bases, Thymine (T) or Cytosine (C), and forming double covalent bond between carbon atoms TT or CC. There are three different dimers distinguished: CPD, 6,4PP and Dewar structure⁽⁵⁾. It is assumed that damage from Dewar structure is not significant and there is 75 % od CPD and 25 % of 6,4PP 1. Most of deoxyribonucleic acid lesions are repaired by the NER (nucleotide excision repair) system and DNA polymerase, but remaining effects are relevant.

Many of biochemical and physical methods used to investigate chemical structure, need an appropriate sample preparation, which often affects structure of the sample and measurement result 1. Moreover, time resolution of these techniques is commonly not sufficient to study the chemical reaction dynamics and investigate its following stages. In this case spectroscopy methods as XAS (X-Ray absorption spectroscopy) and XES (X-Ray emission spectroscopy) are used 1 and taking advantage of XFEL (X-Ray Free Electron Laser) radiation give opportunities to measure sample chemical reaction stages with femtosecond accuracy ⁽⁶⁾.

In order to model UV induced DNA lesions, phosphorus XES spectra calculated with JFEFF 9 software were used. Program allows simulating chemical and quantum parameters that fit best to investigated molecule structure. In following studies best program parameters were found, spectra of reference phosphorus compounds were calculated and compared with experimental results. Next, phosphorus XES spectra and local density of states (LDOS) of UV induced dimers were calculated and analyzed. Theoretical differences between phosphorus XES spectra of damaged and undamaged DNA were obtained and feasibility of future experiments using XFEL was verified.

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Tissue rheology in diagnosis of colon cancer

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In the past decade advances in nanotechnologies and broader cooperation of physical sciences with medicine contributed to discovery of novel markers of disease such as cancers and autoimmune disorders. Cancer development and progression are associated with changes in the mechano-cellular phenotype of cancer and stromal cells, changes in the extracellular matrix structure and composition usually resulting in increased tissue stiffness. Nanomechanical measurements to assess characterization of biophysical properties, such as elasticity of the tissue, performed using atomic force microscope (AFM), became a new standard in molecular and cell biology at nanoscale.

The aim of this study was to use AFM microscope NanoWizard 4 BioScience JPK Instruments and also the Thermo Scientific HAAKE RheoStress rheometer to analyze rheological properties of fresh cancerous and normal human colon tissues taken immediately after surgery. Elastic modulus (i.e. the Young's modulus) of tissues was calculated based on force indentation curves using spherical shape cantilever. Young's modulus was derived from the Hertz-Sneddon model applied to force-indentation curves (Lekka et al., 2012). Rheometer was used for evaluation of rheological properties of larger samples. Measurements of normal force, G' and G" modules as a function of axial and shear strain conditions were made. Mechanical tests were compared with histopathological analysis.

Our results indicate that tumor tissues are significantly stiffer compared to normal tissues and this difference can be noticeable using AFM force spectroscopy, however soft tissues are complex, and their deformability depends on many morphological and physiological features. AFM methods are difficult to applicable to clearly evaluated the elastic properties of larger, complex 3D samples, and determination of their viscoelastic properties is time consuming. Our results showed that the rheometer can provide valuable information about the mechanics of this kind of complex samples and overall, AFM measurements could be employed to complement standard histopathological procedures, but only when combined with bulk examination using shear rheometer.

Superhydrophobic materials for medical applications

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Superhydrophobic surfaces, due to their unique properties, find more and more applications. Coatings with a high wetting angle (over 150 degrees) are used increasingly in the automotive, ship, building, etc. industries. The use of coatings with self-cleaning properties, which are characterized by high resistance to corrosion, is becoming more and more common due to their pro-ecological role and the measurable financial benefits of using them $^{(1)}$. The development of this type of material is closely related to the achievements of nanotechnology. Superhydrophobic surfaces are those in which a combination of two elements is made, namely a hydrophobic material and a specific nano roughness. The superhydrophobic surfaces are referred to as bionics products, or areas that use nature's inspiration in the processes of materials manufacture. In nature, there are a number of examples of surfaces with superhydrophobic properties, the only example cited by the authors examining this kind of materials is the lotus leaf, which can be used to roll drops of water without any resistance while removing any pollution from it. The behavior of drops on the superhydrophobic surface has been described in the theory of Wentzl, Cassie-Baxter, who modified the Young equation with respect to the homo- and heterogeneous nanostructured surfaces $^{(2)}$. Superhydrophobic materials have proved extremely usefulness in a number of biomedical applications, and their introduction to the clinical practice will result in the development of new therapeutic and diagnostic methods. In the field of implant materials, it is valuable that superhydrophobic materials have bactericidal and anti-trombogenic abilities, what makes them suitable for both endoprosthesis and designing materials intended for contact with blood. However, the potential applications of materials with superhydrophobic surfaces can be much wider and include catheters, endotracheal tubes, contact lenses, controlled drug release coatings, and additionally, superhydrophobic materials enable to design and manufacture new systems for supporting and handling microliter-scale droplets in diagnostics.

The purpose of the work was to develop materials with superhydrophobic surfaces for medical applications. The work involved different methodological solutions based on the electrophoresis processes, using both co-deposition and sequential deposition. Carbon nanotubes, nanosilica and polydimethylsiloxane (PDaMS) were used to obtain superhydrophobic coatings. Carbon nanotubes and nanosilica were used to create the specific nanotopography needed in this type of material. The superhydrophobic coatings were made on a metal and carbon substrates. Carbon substrates were made from carbon fibers in the form of nonwovens. Spectroscopic and microscopic studies were carried out and wettability angles were determined. The contact angle of the initial materials ranged from 160-180 degrees. Subsequently, all materials were incubated in body fluids, subjected to bioactivity tests and in vitro degradation studies. Cytotoxicity tests in contact with fibroblast line cells were performed. The results indicated a high potential of the electrophoretic deposition method to manufacture supehydrophobic materials for medical applications.

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Near edge X-ray absorption fine structure spectroscopy with a compact laser plasma source of soft X-rays

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The near edge X-ray absorption fine structure spectroscopy (NEXAFS) is a well-known and established method of material analysis, yielding information about the chemical composition through the measurement of the X-ray absorption spectra near the absorption edge. NEXAFS has been demonstrated using synchrotron radiation and currently almost all synchrotrons have a beamline dedicated for studying the matter using this technique. In the paper we present a compact laboratory system for NEXAFS spectroscopy that was developed using a laser-plasma soft X-ray source. The source is based on a double stream gas puff target irradiated with nanosecond laser pulses. The source was optimized for efficient soft X-ray emission from a krypton/helium target in the range of 1.5 to 5 nm wavelength. The emission spectra for the source and the absorption spectra for the investigated sample were measured simultaneously using a grazing incidence spectrometer. The measurements in the transmission mode reveal the spectral features near the carbon K- α absorption edge of thin samples. The detailed information about the source, the NEXAFS spectroscopy system, the absorption spectra measurements and the results of the studies are presented.

Structural and magnetic properties of alloyed and multilayered FeCu nanowires

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The special magnetic properties, high biocompatibility, low toxicity and relatively low price of Fe nanowires resulted in finding numerous applications in biomedicine, optics, catalysis, and as a perpendicular high-density storage media and sensor devices. Such a wide range of applications requires different properties of nanowires, which can be tailored to special requirements by modification of their morphology, structure or composition.

The FeCu alloyed and Fe/Cu multilayered nanowires were successfully electrodeposited into nanochannels of commercial track-etched polycarbonate membranes. Both of them were prepared by potentiostatic deposition from a sulfate bath of iron and copper ions. The composition of alloys has been modified by adjusting the electrolyte composition, while the multilayered nanowires were produced by alternating cathodic potential applications.

The SEM studies of alloyed and multilayered samples showed arrays of smooth and continuous nanowires with a length of 6 μ m and a diameter determined by the pore size changing for different samples from 50 to 200 nm. The XRD measurements of the alloved FeCu nanowires revealed only peaks characteristic for the Fe phase confirming the polycrystalline bcc structure of nanowires. The same measurements performed for Fe/Cu multilayers indicate a polycrystalline bcc structure but with peaks characteristic for both Cu and Fe phases. TEM studies confirmed a polycrystalline structure of the multilayered nanowires and revealed that indeed the wires are composed of alternating Fe and Cu layers. The elementary composition of nanowires investigated by EDS (energy dispersive spectroscopy) measurements showed an increase in Cu concentration according to the changes in electrolyte composition. The magnetic studies carried out using a SQUID magnetometer showed a magnetic anisotropy of nanowires with an easy axis along the nanowires. The increase in the copper concentration resulted in a decrease of anisotropy energy and coercivity. In multilayered nanowires, an increase of Cu layer thickness caused a decrease of coercivity and non-monotonic changes in anisotropy.

Evaluation of infrared spectral signature associated with pathology as biomarker for chemotherapy efficacy assessment in breast cancer

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Introduction

Triple-negative breast cancer (TNBC) is an aggressive breast cancer subtype with limited treatment possibilities and a poor prognosis. Although TNBC was investigated with different diagnostic techniques, there is still a need for in-depth examination. Fourier transform infrared (FTIR) microspectroscopy is a straightforward, non-destructive and label-free chemical identification modality widely used in biological and medical fields. FTIR spectral features provide molecular information of major biological macromolecules in forms of "biochemical fingerprint", which are crucially important for investigating changes in biological samples such as cells and tissues. With the combination of multivariate data analysis approaches, FTIR microspectroscopy has emerged as a viable diagnostic tool alternative to traditional pathological techniques. The aim of the present study was to monitor the course of chemotherapy in six female patients with the diagnostic approach developed based on focal plane array (FPA) FTIR imaging microspectroscopy and principal component analysis (PCA) approach.

Material and methods

The study was conducted on the basis of formalin-fixed paraffin embedded (FFPE) breast tissue samples obtained from six TNBC female patients before and after preoperative chemotherapy. FFPE breast cancer tissue sections were fixed on CaF2 substrates. Spectra were collected in transmission mode within 4000-800 cm⁻¹ spectral region using a Bruker Hyperion 2000 FTIR microscope equipped with a liquid N₂ cooled 64x64 element FPA detector coupled to a Vertex 70/70v FTIR spectrometer. FPA-FTIR images were analysed using Cytospec v. 1.4.02 (Cytospec Inc., Boston, MA, USA). Principal component analysis (PCA) was subsequently performed using The Unscrambler 10.1 software package (CAMO Software AS., Oslo, Norway). EMSC-corrected second derivative spectra were combined into one set to investigate similarities and differences of the breast tissues before and after the chemotherapy.

Results

The PCA results obtained using the FPA-FTIR spectral data collected from the same patients before and after the chemotherapy revealed discriminatory features that were consistent with the pathologic and clinical responses to chemotherapy. The comparison between healthy and cancerous breast tissues revealed a distinct separation of spectral clusters.

Conclusions

The present findings and analysis indicate that FPA-FTIR microspectroscopy combined with multivariate data analysis has the potential as a monitoring tool for assessing chemotherapy efficacy.

Denoising influence and coherence artifacts reduction in QCL microscope hyperspectral data for the improvement of classification

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The evolution of IR spectroscopy began with single point spectroscopy, but extensive work done within last few years lead to emergence of diffraction limited High Definition (HD) IR Imaging technique alongside with Quantum Cascade Laser (QCL) Microscope. Chemical contrast and high information content make QCL microscope a perfect candidate for clinical applications (e.g. machine learning based cancer detection), nevertheless, a sufficient data quality and measurement throughput must be achieved to reach clinical requirements. The aim of this research was to optimize denoising approaches in order to reduce measurement timescale and improve classification sensitivity. A wide range of spectral and spatial denoising techniques was tested and dominance of multivariate techniques of Principal Component Analysis (PCA) and Minimum Noise Fraction (MNF) was showed ⁽¹⁾. However, denoising only did not provide satisfactory results, with strong coherence and imbalanced illumination effects still present in classification images. Therefore, a custom made algorithm based on Eilers baseline correction was applied, significantly improving classifier prediction.

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Resorbable membranes modified with amphiphilic poly(2-oxazolines) for guided tissue regeneration

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Resorbable membranes can be used in the treatment of periodontal disease according to guided tissue regeneration (GTR) technique $^{(1)}$. In GTR such membrane is used to separate mucous membrane and soft tissue from bone tissue defect and assure required conditions for bone in growth and proper fixation of the tooth root in the bone. After required period of time from implantation, e.g. 6 weeks, the defect is healed, the membrane is degrading and additional surgery is not required. Available GTR membranes are made of collagen or aliphatic polyesters, poly(L-lactide-co-glycolide) (PLGA). To improve biological properties of e.g. PLGA membranes we aimed at modification of their surface with amphiphilic poly(2-oxazolines) (POx)in order to change PLGA chemical state and properties and verify if such modification is not toxic for bone cells. PLGA membranes were made by phase separation in the system PLGA/POx/poly(ethylene glycol)(PEG), followed by PEG leaching. PLGA (85:15, 100kDa, d=1.9), PEG (Mn = 400 Da) and POx (methyl-P[MeOx37-b-BuOx23-b-MeOx37piperidine(P2-P2), Mn = 8kDa, d = 1.14) were co-dissolved in dichloromethane (DCM) at a concentration of 10% wt/vol and 1 wt% POx in respect to PLGA was added. The mixture wascast on glass Petri dishes, followed by air drying for 24 h and vacuum drying for 24 h. Afterwards, PLGA/PEG/POx blends were washed in purified water for 5 days; water was exchanged every 30 min during day 1 and every 2 h during days from 2 to 5. As references PLGA membranes and PLGA foils without POx were made.

FTIR (Nicolet iS5-iD5spectrometer with resolution of 4 cm-1), in attenuated total reflection mode (ATR, with crystal of ZnSe) was usedfor the characterization of main ingredients used in membranes preparation, i.e. PLGA, PEG and POx, as well as obtained PLGA/PEG/POx blend, PLGA/POx membrane and PLGA foil. The samples were assessed in terms of water contact angle values (DSA Mk2, Krüss),microstructure (scanning electron microscopy, SEM, Nova Nano SEM 200, USA).Cytocompatibility was tested in contact with osteoblast-like MG-63 cells. 8x103 cells suspended 1 ml cell culture medium (EMEM,ATTC, USA) supplemented with 10% foetal bovine serum, 1% penicillin/streptomycin, 0.1% amino acids and sodium pyruvate (PAA, Germany) were poured on the samples placed in 48well plate and cells were cultured at 37°C under a humidified atmosphere with 5.0% CO2for 24 and 72 h.

Cell viability was evaluated using Alamar Blue reagent (In VitroToxicology Assay Kit, resazurin based, Sigma-Aldrich) and live/dead staining using 1 ml of PBS supplemented with 1 μ l (1 mg/ml) of calcein AM (Sigma) and 1 μ l (1 mg/ml) of propidium iodide (Sigma). The cells were also stained for phalloidin/DAPI to visualize actin fibers and nuclei, respectively. The samples were washed twice in PBS and observed under a fluorescence microscope (Zeiss Axiovert 40, Carl Zeiss, Germany).

SEM results show that the air-cured (M up, M Pox up) and glass-cured (M down, M Pox down) surfaces of the membranes have porous microstructure (Fig 1). The samples produced with using POx have smaller pores. FTIR results of M Pox showed presence of a bandat about 1620 cm-1, attributed to C=N stretching vibrations from polyoxazolines, which was not observed in the spectrum PLGA foil and PEG. It is a proof that POx is immobilized on the surface of the PLGA membranes. On 24 h MG-63 osteoblast-like cell viability on the membranes was the same as on the foil. On 72h cell viability was higher when cells were cultured on the membranes as compared to control foils. Microscopic observations of MG-63 cells after live/dead staining show that all cells on 24 h and 72 h of culture were stained green, i.e. were alive; no dead cells, i.e. stained red were found. Actin fibres were developed in the highest extent on M down and M POx down. This suggests that PLGA membranes are cytocompatible with model osteoblasts and that presence of Pox does not have a negative impact on cells. In this study we developed a method of manufacturing of porous asymmetric PLGA membranes modified with Pox. The membranes were obtained by phase separation and preferential adsorption of Pox molecules at the interface PLGA-POx-PEG followed by PEG leaching. Surface modification of PLGA with Pox was confirmed with FTIR-ATR. Addition of Pox influenced topography of the membranes, by decreasing average pore size on both sides of the membranes. All membranes were cytocompatible with osteoblast-like cells. Presence of POx resulted in improved cell adhesion as shown by microscopic studies after fluorescence staining for nuclei and cytoskeleton actin fibers. To sum up, one-step phase separation process between PLGA, PEG and POx, dissolved in DCM followed by drying and PEG leaching resulted in cytocompatible, asymmetric PLGA membranes, which might be considered for guided tissue regeneration technique in periodontology and in bone tissue engineering.

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Monolayers of noble metal nanoparticles on colloidal carriers

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Formation of positively charged gold (AuNPs) and silver (AgNPs) nanoparticle layers on polystyrene (PSMs) and silica (SiO₂Ps) particles was studied using electrokinetic methods, atomic force microscopy (AFM) and scanning electron microscopy (SEM) $^{(1,2)}$. Primarily, the dependence of the electrophoretic mobility of the particles on the nanoparticle concentration in the suspensions was determined for various ionic strengths. These results were quantitatively interpreted in terms of the three-dimensional electrokinetic model. This allowed to derive a formula for calculating the coverage of nanoparticles under in situ conditions whose validity was confirmed by direct SEM imaging of deposited nanoparticle layers (Fig. 1). Additionally, the maximum coverage under different conditions was determined using a concentration depletion method based on AFM imaging of residual nanoparticles deposited on the silicon substrate. The maximum coverage of the nanoparticle monolayers increased with ionic strength attaining a value of 0.35 for ionic strength of 3×10^{-3} M. This effect was attributed to the decreasing range of lateral electrostatic interactions among deposited nanoparticles. The electrokinetic properties of the nanoparticle layers were also evaluated in pH cycling experiments that confirmed their stability.



Fig. 1. Typical SEM micrograph presenting the AuNP monolayers formed on the $PSMs^{(1)}$.

The AuNP monolayers deposited on the SiO_2Ps were applied as active substrates for detection of rhodamine B using surface enhanced Raman spectroscopy (SERS). On the other hand the SiO_2Ps and the PSMs covered by the AgNPs exhibited strong toxicity towards histiocytic lymphoma (U-937) and human promyelocytic (HL-60) cell lines. Beyond significance to basic science, the new data acquired in this work confirmed the feasibility of preparation of the metal nanoparticle layers with controlled structure, coverage, and electrokinetic properties⁽¹⁾.

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Application of premature chromosome condensation and dicentric analysis in retrospective biological dosimetry of radiation accident

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Cytogenetic dosimetry based on dicentric analysis (CA) and premature chromosome condensation (PCC) plays an important role in the triage and medical management of affected people in radiological $\operatorname{accidents}^{(1)}$. In our studies, blood samples from persons that were suspected of accidental exposure to ionizing radiation during interventional radiology (IR) procedure were investigated for the purpose of the retrospective biological dosimetry of absorbed dose. In this case the obligatory reported dose value, KAP (Kerma Air Product), was very high: 10.6 [Gyxm2]. The skin dose was evaluated as 17 Gy. Due to the lack of the possibility to relationship KAP with an effect (KAP could be connected with the maximum local dose in the X-ray field) the patient's blood and 2 mostat- risk people (medical doctors) were investigated. In addition, 5 dosimeters for the whole body (Hp (10)) and 1 ring dosimeter measuring the skin exposure (Hp (0,07)) of medical workers participating in the radiological procedure were investigated. The measurements of individual doses by the thermoluminescent dosimeters (TLD) were carried out by the Laboratory of Individual and Environmental Dosimetry (Polish acronym LADIS). To estimate the potential absorbed dose lymphocytes from blood were analysed for the presence of chromosomal aberrations (dicentrics and rings), which are the "gold standard" assay for biodosimetry. Additionally, absorbed dose was monitored by the analysis of excess fragments with PCC technique, which is recommended for high doses and partial body exposure. Finally, estimated doses for obtained blood samples were compared to the dose response curves for dicentrics and PCC excess fragments, detected in our laboratory after induction in human lymphocytes by in vitro X-ray irradiation $^{(2)}$.

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How to investigate drugs distribution within colloidal nanocarriers mono-layer: label free characterization by AFM-IR

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Novel approaches to improve cancer therapy assume application of metallic nanoparticles as an efficient drug delivery system⁽¹⁾. This strategy requires designing stable drug/nanocarriers conjugates that can effectively interact with the target site. It is also important to investigate more deeply into the understanding of how the drug interacts with the carrier and assessment of the drug distribution on the potential carrier surface^(2,3).

In this study, infrared (IR) nanospectroscopy called AFM - IR was employed for characterization of adsorption geometry of erlotnib and gefitinib (antitumoral drugs) onto silver and gold nanocarriers mono-layer. This hybrid technique provides information about the topography of samples with nanoscale spatial resolution typical for atomic force microscopy (AFM) together with the chemical characterization (molecular composition) ensured by IR spectroscopy ^(4,5). The obtained results indicating functional groups involved in the adsorption process correspond with the surface - enhanced Raman spectroscopy (SERS) data received previously on the same system⁽²⁾. Moreover, the AFM - IR technique provides accurate image of the investigated drug location on the applied monolayer.

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Insight into molecule binding to the metal nanostructure

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Infrared (IR) and Raman (RS) spectroscopic techniques are very useful tools to study molecular structure of different types of compounds. Nevertheless, the molecule organization may change noticeably upon adsorption onto roughened metallic nanostructure $^{(1)}$. The most widely used techniques for monitoring the interfacial behaviour of molecule-metal conjugate are surface-enhanced Raman (SERS) and surface-enhanced infrared absorption (SEIRA) spectroscopies $^{(2)}$. However, the last few years have shown that there is a growing interest in studying the adsorption phenomenon at the nanoscale level using atomic force microscope infrared-spectroscopy $(AFM-IR)^{(3)}$. This work describes the subtle variations in adsorption geometry of anticancer drugs/potential drugs after conjugation with metal nanosensors using aforementioned SERS and SEIRA techniques. Additionally, the influence of different incidence angles in SEIRA on spectral changes was explored. Furthermore, to better understand the molecule-metal interaction and to achieve nanoscale spatial resolution, two orthogonal polarization modulations in AFM-IR nanospectroscopy were employed. The comprehensive analysis employing the aforementioned vibrational spectroscopy techniques provided a detailed description of biologically active molecules after immobilization onto selected metal nanosubstrates.

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Ion implantation in diamonds for efficient creation of NV⁻

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The discovery of negatively charged nitrogen vacancies (NV^-) in diamonds opened up additional exciting applications, for example in biophysics or quantum information^(1,2). These colour centres are sensitive to the changes of a magnetic field. When the centres are excited, the changes can be read and quantified. The sensitivity of such magnetic sensors depends on the concentration of (NV^-) and for different applications it needs to be appropriately adjusted.

The colour centres were fabricated in single-crystal and polycrystaline diamonds by means of N⁺ implantation with doses ranging from 1×10^{13} to 5×10^{17} ions/cm². This process increases the amount of nitrogen and creates additional vacancies available to transform into NV⁻. In order to finish the process, heat treatment was applied at 750 °C for two hours in air to increase diffusion and the recombination rate of nitrogen and vacancies.

The diamonds were analysed by Raman spectroscopy, fluorescence and Optically Detected Magnetic Resonance $(ODMR)^{(3)}$.

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Electrophysical properties of granular film alloys as elements of sensor electronics

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The search for film materials with improved properties is stimulated by their high functionality, wide application in the creation of thermistors, strain sensors and sensors of magnetic field. Film materials must have a thermal stability of structural-phase composition and stable characteristics in the working range of temperatures, strain and magnetic field. The purpose of this work was a complex study of electrophysical properties, which remain poorly understood, in correlation with the structural and phase state of two-component film systems based on Co and Ag, Co and Cu, Fe and Cu, which can be used as sensitive elements of thermistors and temperature sensors.

Two-component film systems based on Co and Cu or Ag and Fe and Cu were obtained in a vacuum chamber ($p = 10^{-4}$ Pa). The condensation of Fe and Cu or Ag films was carried out by a resistive method of evaporation, and Co films were electron-beam. The deposition of films took place as a simultaneous sputtering of two sources, and by alternating condensation of the two components. In the case of systems with limited mutual solubility for the formation of solid solutions methods of simultaneous condensation of metals (systems based on Co and Ag) or layered condensation of superfine layers (systems based on Fe and Cu) were used. In the case of systems with unlimited mutual solubility, granular (Cu, Co) solid solutions were obtained by the method of layered condensation with followed annealing. The formation of granular films was carried out as a layer condensation of superfine layers (d = 0.5-3 nm) with subsequent annealing up to 850 K, and simultaneous condensation of separate components. With a total thickness of films up to 60 nm, the average size of Co magnetic granules is 3-7 nm. Parameters of the fcc lattice of a granular s.s. is a = 0.408-0.409 nm (based on Ag and Co) and a = 0.358 nm (based on Cu and Co). In multilayer films based on α -Fe and Cu formed non-granulated s.s. based on α -Fe (at $1.5 < d_{Fe} < 2$ nm) or s.s. based on Cu (at $d_{Fe} < 1.5$ nm) with lattice parameters which are very close to the α -Fe or Cu parameter. Studies of electrophysical properties indicate that the resistivity depends to a large extent on the total concentration of the magnetic component and the temperature of the measurement. The value ρ in thermostabilized films is $(1-4) \times 10^{-7} \ \Omega \times m$, and the value of the thermal coefficient of resistance TCR = $(0.5-1.5) \times 10^{-3} \text{ K}^{-1}$.

As a result of the complex study of the structure-phase state and electrophysical properties (resistivity, temperature coefficient of resistance) of film systems based on Co and Cu or Ag, Fe and Cu, the following is established. In film systems, obtained by a layered condensation with subsequent annealing or simultaneous condensation, granulated alloys with an average size of granules up to 10 nm are formed and the lattice parameter is close to the corresponding value for the base component. For the first time, systematic studies of the dependence of TCR versus temperature and atoms of the magnetic component concentration have been investigated. The obtained dependences have typical character for metal films, that is, linear dependence on the concentration and inversely proportional to temperature.

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XRD diffraction studies of hydroxyapatite coatings implanted with silver ions)

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Hydroxyapatite (Hap) is a material widely used in orthopedic surgery due to its unique properties such as biocompatibility, bioactivity and osteoconduction. It has a composition similar to the inorganic phase of the bone tissue, and promotes the desired tissue response accelerating bone growth around the implant. Its use reduces discomfort after surgical endoprosthetic procedures. Despite these positive features HAp does not have internal antibacterial protection. Recently, the problem of resistance of many bacterial strains to antibiotic therapy is broadly studied. The presence of bacteria around the implant can lead to unwanted infections. This problem stimulates the development of functional materials that provide adequate internal antibacterial protection. Enriching hydroxyapatite with silver nanoparticles has become a fairly common method of improving the bactericidal properties of biomaterials. Silver has strong activity against a broad spectrum of bacteria, including those resistant to antibiotics. However, the issue of toxicity remains unclear in this case. The ion implantation method limiting the mobility of Ag ions can become an effective way to improve the biocompatibility of HAp-Ag systems.

Our research is based on the fabrication of crystalline hydroxyapatite coatings on modified titanium substrates using the hydrothermal method. The Ti/TiO2/HAp system was next implanted with silver ions using an ion source with energy of 25 keV. Implantation was performed for four different fluences of 1×10^{16} , 3×10^{16} , 5×10^{16} and 6×10^{16} ions/cm². We examined morphological and structural changes of Ti/TiO₂/HAp resulting from Ag implantation. Surface morphology of Ti/TiO₂/HAp samples before and after implantation was observed by SEM. Detailed structural analysis was carried out using XRD diffraction and Raman spectroscopy. Our results showed that the crystal morphology of HAp does not change with ion fluence increase. Based on the XRD data, we did not observe after implantation additional phases formation or changes of the crystal lattice constants of the hexagonal HAp structure. On the other hand the XRD analysis demonstrated that ion implantation introduces defects seen as the broadening of diffraction peaks with the increase of Ag ion fluence.
Application of X-ray reflectometry in analysis of Ti and TiO_2 nanolayers implanted with Xe^{q+} ions

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Influence of pulsed laser interference heating process on magnetic properties and structure of ironbased amorphous ribbon are reported. Laser interference heating allows creating periodically placed laser heated micro-areas. In the laser affected microareas, structure and magnetic properties changes occur. To compare obtained results the samples after conventional crystallization were prepared by annealing at 600°C. Microstructure characterization by electron microscopy showed that the laser beam energy cause the partial crystallization of amorphous material. Partial crystallization affect on magnetic properties of material. Magnetic hysteresis loop measurement by SQUID magnetometer showed the difference in saturation magnetization with unchanged remanence. Magnetization of material in single laser heated microareas was determined by magnetic force microscopy. Investigations showed the differences in magnetic structure of amorphous material and laser affected material.

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Femtosecond dynamics in disordered systems probed with the use of 4^{th} generation X-ray sources

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Introduction of 4th generation X-ray sources opens new possibilities in exploration of the area of X-ray science. Ultra-short X-ray pulses delivered by X-ray Free Electron Lasers (XFEL) or Plasma X-ray Sources (PXS) allows for tracking of matter transformations in physical, chemical and biological systems with exceptional time-resolution. Moreover, application of ultra-bright and tightlyfocused XFEL beams gives opportunity to create atomic states with a unique electronic configuration via the non-linear interaction of photons with matter. Combination of femtosecond X-ray pulses with X-ray penetrating properties and capability to probe atomic states with elemental selectivity, gives opportunity to address a number of fundamental and applied research questions. We will report on the use of XFELs and PXS sources to study dynamics in disordered systems as well as to explore nonlinear processes of X-ray interaction with atoms and molecules. Several projects will be presented together with experimental results obtained at Linac Coherent Light Source (USA), SwissFEL (CH) and SACLA (JP) facilities. We will also discuss application of X-ray spectroscopy methods with Plasma X-ray Sources at Extreme Light Infrastructure (ELI, CZ) to probe chemical and biological interactions at in-situ conditions.

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X-ray coherence tomography (XCT) with 2 nm axial resolution using a compact laser plasma soft X-ray source

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We present a nanometer resolution optical coherence tomography (OCT) using broadband soft X-ray radiation (SXR), often called X-ray Coherence Tomography (XCT), with 2 nm axial resolution using a compact laser plasma soft X-ray source. The laser-produced plasma was formed by the interaction of nanosecond laser pulses with a gaseous target in a double stream gas puff target approach. The source was optimized for efficient SXR emission from the krypton/helium gas puff target in the 2 to 5 nm spectral range, encompassing the entire "water-window" spectral range from 2.3 nm to 4.4 nm wavelength. The coherence parameters of the SXR radiation allowed for the XCT measurements of a bulk multilayer structure with 10 nm period and 40% bottom layer thickness to period ratio, with an axial resolution of about 2 nm and detect multilayer interfaces up to a depth of about 100 nm. The experimental data are in agreement with the XCT simulations performed on ideal multilayer structure. In the paper, detailed information about the source, its optimization, the optical system, XCT measurements and the results are presented and discussed.

Kinetics of oxidation and antioxidation processes in biological solutions observed by NMR relaxation

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Oxidation processes in the human body cause an increased risk of many chronic diseases. It is recommended to monitor and regulate the blood redox potential by measuring levels and activities of endogenous antioxidants. In recent works, we used the NMR relaxation method to measure the time changes of T1 relaxation time (named "time courses") after initiating the oxidation process by adding 3% hydrogen peroxide to blood serums. Time courses observed in aqueous protein solution (like egg white or bovine serum albumin) were well fitted by exponential decays with parameters dependent on type and concentration of proteins ((1)). Adding an antioxidant (e.g. ascorbic acid or glutathione) to protein solution resulted in increase of the relaxation time after reaching the minimum. Similar non-exponential time courses were observed in native blood serums which contained the endogenous antioxidants ((1, 2)). In this study the time courses of relaxation times were fitted by combination of exponential and compressed exponential functions. The type of used function depended on the kinetics of oxidation processes and the activity of natural and added antioxidants.

The presented models of time courses of NMR relaxation times may be a good tool for better understanding of oxidation processes in biological materials. In the future, with the help of relaxation time measurements in NMR tomography, it may be also possible to investigate these important processes in vivo.

Fourier transform infrared spectroscopy for monitoring of the cholesterol oxidase enzyme structure

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The oscillation spectroscopy techniques including Fourier Transform Infrared Spectroscopy (FTIR) and Raman spectroscopy, are powerful methods for biological molecules analyzing and provide a wealth of information on structure, interactions and mechanism of reaction⁽¹⁾. The main problem for the enzyme characterization is using very small amounts of enzyme, below the detection capabilities. The Surface Enhanced Raman Scattering Spectroscopy (SERS) dramatically increases the sensitivity of measurement, but it requires a suitable SERS carrier⁽²⁾.

Cholesterol oxidase (ChOX) is a flavin adenine dinucleotide (FAD) dependent enzyme, which catalyzes the oxidation and isomerization of cholesterol. ChOX is one of the most important enzyme in medical purposes⁽³⁾ and it is using for the determination of the serum cholesterol content in clinical diagnostics. Cardiovascular diseases are the most common cause of disability and mortality (32.26% of death in 2016) and high cholesterol level is estimated as one of the main risk factors causing numerous deaths (4.39 million of death in 2016). The ChOX was characterized by FTIR techniques. Infrared spectra were obtained for three different forms of enzyme samples: solid, suspended in phosphate buffer, and conjugated with the gold nanoparticles (AuNPs). Observed vibrational lines are attributed to chemical bonds of amino acid side chains as well as protein secondary structure. The obtained data allows to identify the changes that occur depending on the close environment of the enzyme.

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Denoising influence on FT-IR imaging data histologic classification of pancreatic tissue

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Proper denoising approaches are crucial for speed optimization of imaging techniques⁽¹⁾ and recently we have compared state of the art algorithms⁽²⁾ in terms of SNR gain and Signal Distortion. However, for a histological classification problem these metrics may not reflect the actual power of the dataset, as machine learning algorithms often look at very small features, which are not obvious to the naked eye. To properly test out the influence of denoising on the classification models we have compared the classification accuracy of Random Forest models after treatment with the best noise removal algorithms⁽³⁾. Moreover, the size of the dataset is expected to influence the multivariate denoising methods efficiency and results of varying the image size will be investigated for Principal Component Analysis (PCA) and Minimum Noise Fraction (MNF) methods.

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Electrical transport properties of metal/metal-oxide/metal films prepared with anodization process

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The electrical transport properties of multilayered metal/metal oxide/metal films (i.e. Ti and Fe) are the main concern of this studies. The sample preparation include a layer of Ti or Fe deposited on Si wafer and next anodization of top part of metal, where as a result a thin layer of porous metal-oxide is obtained. On top of oxide layer a second metallic layer of Ti or Fe is deposited. Therefore a four different types of multilayered films are prepared, i.e. four double metal/metal-oxide junctions: Ti/Ti-O/Ti, Ti/Ti O/Fe, Fe/Fe-O/Ti, and Fe/Fe-O/Fe. Additionally layers of gold situated at the bottom and on the top of the samples are used as a contact electrodes.

The anodization process allows for creation of porous oxide layer in an amorphous form. Transformation and creation of a crystalline oxide layer of Ti-O or Fe-O is performed with additional annealing at high temperature of 673K in vacuum for 15 minutes.

The studies of electrical transport properties include magnetoresistance measurements and I-V characteristics at ambient and at low temperatures (300 and 5K) for the four types of junctions before and after annealing. The comparison of obtained results for amorphous and crystalline samples and different kinds of porous junctions will be presented. Additionally XRD studies and morphology analysis will be demonstrated.

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