Functional Thin Films and Surfaces
Room Palm 1-2 - Session MB3-1-ThM

Nanomaterial-based Thin Films and Structures I

Moderators: Ondrej Kylian, Charles University, Prague, Czechia, **Jörg Patscheider**, Evatec AG, Switzerland

8:00am **MB3-1-ThM-1 Dual Scale Structures Based on Nanocolumns and Nanoparticles**, ***Lidia Martinez (lidia.martinez@icmm.csic.es)***, ICMM-CSIC, Spain; *J. García-Martín,* IMN-CSIC, Spain; *Y. Huttel,* ICMM-CSIC, Spain
INVITED

Like the formation of alloys that combines the properties of different elements resulting in novel materials, the combination of different shapes and dimensions also leads to materials having novel properties, especially at the nanoscale. We will first briefly present the ultra-high vacuum physical methods used to grow the Nanocolumns (NCs) by Glancing Angle Deposition (GLAD) [1-2] and Nanoparticles (NPs) fabricated by means of a Multiple Ion Cluster Source (MICS) [3-4], highlighting the control over chemical composition, shape and dimensions of the fabricated nanostructures.Later, we will present some examples where the combination of NCs and NPs leads to synergic effects using materials like gold, silver, titania or iron oxide. In particular, we will present some examples of application as antibacterial coatings [5], photo-induced self-cleaning surfaces [6], SERS substrates [7], controlled wettability or catalysis among others.

References:

1. R. Álvarez et al., “Antibacterial Nanostructured Ti Coatings by Magnetron Sputtering: From Laboratory Scales to Industrial Reactors”, Nanomaterials 9, 1217 (2019).

2. J. M. García-Martín et al., “Tilt angle control of nanocolumns grown by glancing angle sputtering at variable argon pressures”, Appl. Phys. Lett. 97,173103 (2010).

3. "Gas Phase Synthesis of Nanoparticles", Wiley-VCH Verlag GmbH, 2017, Ed. Y. Huttel.

4. D. Llamosa et al., “The ultimate step towards a tailored engineering of core@shell and core@shell@shell nanoparticles”, Nanoscale 6, 13483 (2014).

5. D. Medina-Cruz et al., “Synergic antibacterial coatings combining titanium nanocolumns and tellurium nanorods”, Nanomedicine: Nanotechnology, Biology, and Medicine 17, 36–46 (2019).

6. F. Fresno et al., “Photo-Induced Self-Cleaning and Wettability in TiO2 Nanocolumn Arrays Obtained by Glancing-Angle Deposition with Sputtering”, Adv. Sustainable Syst., 2100071 (2021).

7. G. Barbillon et al., in preparation.

8:40am **MB3-1-ThM-3 MGA Nanoparticle Thin Films for Enhanced Hydrogen Gas Sensing: Synthesis, Modeling, and Characterization**, ***Stanislav Haviar (haviar@kfy.zcu.cz)***, *T. Kozák, K. Shaji,* University of West Bohemia, Czechia; *T. Košutová,* Charles University, Czechia; *B. Prifling, V. Schmidt,* Ulm University, Germany; *J. Čapek,* University of West Bohemia, Czechia

Thin films formed by nanoparticles from various metal oxides (WO_x, CuO_x, PdO_x) were synthesized using a magnetron-based aggregation cluster source (MGA). The mixing ratios of the oxide particles were adjusted to achieve the best conductometric sensorial response toward hydrogen gas.

(i) Single-material films were investigated utilizing electron microscopy, energy dispersive and photoemission spectroscopies and small-angle x-ray scattering (SEM, TEM, EDS, XPS, SAXS).

(ii) Results of these analyses were used as an input for hard-sphere packing algorithm simulations generating models of synthesized mixed-materials films.

(iii) Optimized finite element modeling was used to calculate the conductivity of modeled films. Various material parameters were adjusted to receive a quality estimation of mixed-materials behavior.

(iv) Output of the simulation was used as a lead for synthesizing films with optimum ratios of materials to generate nanoheterojunction-rich materials.

(v) Promising candidates were assembled as conductometric gas sensors and tested towards hydrogen gas.

In the talk, the details of MGA system orchestration will be discussed. Special attention will also be paid to the simulation strategy and the process of simulation results verification.

See illustrative figures in the Supplemented file.

[1] Batková; Kozák, T.; Haviar, S.; et al. *Surf. Coatings Technol.* 2021, **417**

[2] Haviar, S.; Čapek, J.; Batková, Š.; et al. *Int. J. Hydrogen Energy* 2018, **43**

[3] Shaji, K., Haviar, S., Zeman P et al. *Surf. Coatings Technol.*Controlled sputter deposition of oxide nanoparticles-based composite thin films, *submitted*

9:00am **MB3-1-ThM-4 Enhanced Dimer Sputtering and Production of Nanoparticles by Pulsed Magnetron Discharge**, *P. Čurda,* University of South Bohemia, Czechia; *R. Hippler,* University of Greifswald, Germany; *M. Cada,* Institute of Physics, Czech Academy of Sciences, Czechia; ***Ondřej Kylián (ondrej.kylian@gmail.com)***, Charles University, Czechia; *Z. Hubicka,* Institute of Physics, Czech Academy of Sciences, Czechia; *V. Stranak,* University of South Bohemia, Czechia

This study investigates the initial stage of nanoparticle formation in physical vapor deposition processes, emphasizing the role of atomic dimers as cluster nuclei. The process of metal nanoparticle formation and growth by gas aggregation starts with the release of free metal atoms and nuclei through magnetron sputtering followed by thermalizing collisions and by atom attachment and coagulation. By employment of energy-resolved mass spectrometry and scanning electron microscopy imaging, dimers originating in the discharge gas phase ($ArCu^+$, Ar_2^+) and dimers sputtered directly from the target (Cu_2^+) were examined. Our findings reveal that sputtered Cu_2^+ dimers which carry the high-energy tail of the Thompson distribution play a crucial role as nanoparticle nuclei. Haberland’s concept aggregation source confirmed that the population of Cu_2^+ dimers is directly proportional to the mass transported by nanoparticles. The gas aggregation process can be optimized for enhanced nanoparticle production by the employment of a pulsed discharge, which leads to increased energies of impinging Ar ions and enhanced sputtering of metal dimers. There exist optimal conditions, where the dimer production is increased, but the plasma is not too hot for the nuclei and nanoparticles to decay. Under such conditions, the production rate can be increased by a factor of 10. This enhancement in nanoparticle yield is achieved with the same invested power as for the DC sputtering. Furthermore, the proposed mechanism and the role of dimers may be material-independent, as qualitative agreement was also observed for Ag nanoparticles. This research contributes to a deeper understanding of the fundamental mechanisms governing the early stages of nanoparticle synthesis through physical vapor deposition.

Acknowledgment
The research was financially supported by the Czech Science Foundation through the project GACR 21-05030K and by the Ministry of Education, Youth and Sports of the Czech Republic through the project “Solid state physics for the 21st century” CZ.02.1.01/0.0/0.0/16_019/0000760.

9:20am **MB3-1-ThM-5 Plasma Polymer - Ag Nanocomposites: Is the Gas Aggregation Source of Nanoparticles an Appropriate Technique for Their Synthesis?**, ***Zdenek Krtous (krtousz@gmail.com)***, *T. Kosutova, P. Pleskunov,* Charles University, Prague, Czech Republic; *B. Baloukas, L. Martinu,* Polytechnique Montréal, Canada

Metamaterials or metasurfaces represent the emerging field of nanotechnologies focusing on pushing the limits of the standard optical coatings. One of the most promising types of metamaterials are plasmonic nanocomposites based on metallic nanoparticles. The usefulness of such materials was demonstrated for absorbers, plasmonic coloration, transparent electrodes and optical filtering. In this project, we investigate a classical type of plasmonic metamaterials – silver nanoparticles embedded in a plasma polymer matrix, prepared by simultaneous co-deposition of both organic and metallic components. The organic matrix is prepared by the recently developed Plasma Assisted Vapour Thermal Deposition (PAVTD). The PAVTD allows one to control the chemical composition and, as a result, the optical and mechanical properties of the matrix within a wide range. We investigate two different cases of synthesis of metallic nanoparticles. In the first case, which could be considered a more classical approach, the nanoparticles are formed by co-deposition of silver atoms by magnetron sputtering. The silver atoms form nanoparticles inside the polymeric matrix. The growth rate of the matrix limits the size of the growing inclusions. In the second case, the Gas Aggregation Source (GAS) was used to fabricate nanoparticles in the gas phase. Subsequently, pre-fabricated nanoparticles are landing on and being embedded into the growing matrix. Due to the different nanoparticle growth mechanisms, the

optical properties of such nanocomposites are not equivalent even at similar filling factors. Finally, the applicability of the PAVTD – GAS films is demonstrated by the fabrication of a nanocomposite-based Bragg´s reflector.

9:40am **MB3-1-ThM-6 Fabrication of Ag-modified $BaTiO_3$ Nanorod Arrays and their Properties of Piezo-Photoelectric Catalysis**, ***Yu-Han Hsu (emilyanna5428@gmail.com)***, *K. Chang, Y. Chiu,* National Cheng Kung University (NCKU), Taiwan

α-Fe_2O_3 is an attractive n-type semiconducting material in the visible-light photocatalytic application because of its characteristic of narrow energy band gap characteristics for absorbing the visible light. The optical property can be tailored through morphology control, elemental doping, or compositing with other materials. However, studies on the α-Fe_2O_3 nanorod arrays with the metalic nanoparticles directly through hydrothermal processes for the fabrication still lacking. In this study, well-aligned α-Fe_2O_3 nanorod arrays/Au nanoparticles were synthesized through a facile hydrothermal reaction and solution-based method. To optimize the morphology of Fe_2O_3 nanorod arrays for compositing with Au, hydrothermal parameters, including concentrations and types of precursor solutions, reaction time, and temperatures, were manipulated. And then, it composited with different amounts and sizes of Au nanoparticles, finding an optimized condition for the visible-light photocatalytic application with the LSPR effect from nanogold. X-ray diffraction and scanning electron microscopy were employed to determine the phase and morphology of the resultant composite samples. In addition, the interfaces between the materials were observed from the transmission electron microscopy. Uv-vis spectroscopy was utilized to measure the absorption and the energy band gaps of the materials, which were significant for building the energy band diagram of the system. The composites were further used in the visible-light photocatalytic application.

Keywords: α-Fe_2O_3 nanorod arrays, Au nanoparticles, hydrothermal reaction, LSPR, visible-light photocatalysis

10:20am **MB3-1-ThM-8 Combinatorial Approach of Zr-Ti-Al Thin Films: Understanding Glass-Forming Behavior, Morphological Changes, and Thermal Stability**, ***Zil Fernández-Gutiérrez (zil.fernandez-gutierrez@univ-lorraine.fr)***, *D. Pilloud, S. Bruyère, S. Hupont, J. Pierson,* Institut Jean Lamour - Université de Lorraine, France

The advancement of nanotechnology relies significantly on developing thin film metallic glasses (TFMGs), given their distinct attributes such as high strength and corrosion resistance at the atomic level. The exploration of new TFMG systems holds the potential to revolutionize technology, enhancing performance and durability across applications in electronics, coatings, and medical devices. In this study, we employed a combinatorial approach to investigate the glass-forming ability of Zr-Ti-Al thin films synthesized through magnetron co-sputtering. Our findings demonstrate that controlled variations in chemical composition influence the amorphous or crystalline state of the layers, with an observed reduction in grain size with increasing the Al content. The SEM images illustrate notable modifications in surface and cross-sectional morphology. However, despite the glassy form, electrical property determinations reveal that TFMGs maintain consistent electrical characteristics with their ternary crystalline counterparts of Zr-Ti-Al films. Values ranging between approx. 100 and 200 μΩ·cm have been measured for either crystalline or amorphous films. Lastly, the thermal stability of Zr-Ti-Al TFMGs was assessed through TEM and Raman analyses following annealing processes. The crystallization starts at temperatures higher than 300 °C. Since the annealing has been performed in air, the formation of oxides (ZrO_2 and TiO_2) has been evidenced by Raman.

10:40am **MB3-1-ThM-9 The Impact of Laser Annealing on Electrical Resistivity and Mechanical Properties in Highly(111)-Oriented Nanotwinned Ag Thin Films**, ***Tsai-Shaun Kuo (shirlley.kuo2000@gmail.com)***, *C. Yang, F. Ouyang,* National Tsing Hua University, Taiwan

Recently, with the trend of miniaturization in microelectronic devices, resistivity plays a crucial role in the performance of electronic devices. Isothermal furnace annealing is usually conducted to enable grain growth to possess lower resistivity on interconnects; however, furnace annealing is usually time-consuming. By approach of locally abnormal grain growth, the electrical resistivity could be much more improved and still remains good mechanical properties.

In this study, we proposed using laser annealing to facilitate the grain growth on the highly (111)-oriented nano-twinned Ag thin film. The laser pulse frequency was fixed at 100 Hz, the pulse width was fixed to 1 ms and the laser is incident from the side of the silicon substrate to heat the film in purpose to avoid high reflectivity of the silver thin film surface. The laser annealing experiments were conducted with low laser annealing power (8.54, 16.44, 19.08, 24.35 W) in long annealing time (3 and 5 minutes) or high laser annealing power (50, 60 W) win short annealing time (4-10 seconds). For temperature controlment, the thermal couple was used to measure the temperature in the central of substrate during the laser annealing process. Dual-beam focused-ion beam system (FIB) was used to observed the cross-sectional microstructure images of as-deposited and laser annealed silver films. And the surface orientation was analysed by electron backscatter diffraction (EBSD). X-ray Diffractometer (XRD) was introduced in detecting the preferred orientation. The surface microstructure was investigated by Scanning electron microscope (SEM). Finally, four-point probe was used to detect the resistivity and Nanoindenter (NIP) was used to study the hardness.

Exceptional abnormal grain growth of Ag films can be achieved at 210 ℃ in 3 min, being much faster and lower temperature than furnace annealing. The microstructural and property evolution during laser annealing and the corresponding mechanism were discussed in detail below.

11:00am **MB3-1-ThM-10 Stainless-steel Nano-Pyramid Structure Coating to Enhance Oil/Water Separation**, ***Helmi Son Haji (d11104807@mail.ntust.edu.tw)***, *J. P. Chu,* National Taiwan University of Science and Technology, Taiwan

The process of separating oil and water is crucial for modern human life. Oil waste can affect living environments and impact human health. Various industries require breakthroughs in this field, including the food, petrochemical, oil mining and semiconductor industries. The urgent need for oil waste treatment causes a growing focus on the research of oil effluent. An oil-water separation process's scalability, efficacy and efficiency are crucial factors in the successful purification of oily wastes. Therefore, this research proposed a highly scalable, low-cost production method for fabricating membranes with outstanding selectivity and permeability. The proposed membrane comprises mixed cellulose ester (MCE) with stainless steel (SS) nano-pyramidal structure coating on its surface. The unique morphological characteristics of nano-pyramidal stainless-steel coating exhibit superhydrophilic properties and superoleophobic underwater, which prevent oil adhesion and enable exceptional oil separation performance, achieving an impressive efficiency of up to 99% in the process of filtering oil with various solutions, reaching high recyclability up to 99% in four cycles, also have good stability performance at low until high temperature (60°C), and compatible with diverse environmental conditions from acidic (pH 1) to alkaline (pH 14) [1].

Keywords: Stainless-steel, Coating, MCE.

11:20am **MB3-1-ThM-11 Study of Interfacial Reactions in Artificially Nanolayered Mg-Mo-N Thin Films**, *B. Julien,* ***Andriy Zakutayev (andriy.zakutayev@nrel.gov)***, National Renewable Energy Laboratory, USA

Ternary nitrides are an exciting class of materials for various applications such as hard coatings, LEDs, magnets, superconductors, or topological materials. Many of the most interesting nitride phases are predicted to be metastable. In bulk synthesis, reactions necessary occur at the interfaces, and so solid-state diffusion is required to drive complete nucleation. This leads to condition of high temperature and long-time reactions, which can bypass metastable phases.

Thin-film synthesis of ternary nitrides often leads to cation-disordered structure yet predicted unstable by thermodynamics calculation. Post-deposition thermal annealing can sometimes overcome energetic barriers and lead to nucleation of the layered targeted phase. However, the kinetic window is often narrow and requires high temperatures to trigger atomic diffusion. Therefore, nanolayered thin-film structures with designed diffusion lengths and interface densities offer an opportunity to overcome this situation.

To investigate the interfacial nucleation, we propose to reduce the atomic diffusion length (typically ~1um in bulk synthesis) by fabricating multilayer nanolaminate structures of the binary precursors, as a model system. Post-deposition annealing, interlayer thickness, and the multilayer period modulation are studied as a mean to control the structural properties of the nitride thin films.

In this study, we focus on the Mg-Mo-N system, in which $MgMoN_2$ phase is predicted to be thermodynamically stable and exhibits a natural layered structure built up by alternating layers of edge-sharing MgN_6 octahedra and MoN_6 trigonal prisms. This makes it a good candidate for this work as in a

thermodynamics point of view, the structure tends to naturally form a layered structure and should be more favorable to nucleate from a layered precursor.

The nanolayered films are fabricated by RF co-sputtering, using a computer-controlled sputtering chamber featuring programmable shutters in front of each sputter cathode, allowing us to control the modulation sequence during the deposition. One major challenge here is to minimize the interfacial roughness during the deposition, limiting the intermixing at the interfaces. Once co-calibration of deposition rate and composition is established for both binary phases, a set of multilayer films with different modulation period and composition are characterized by X-ray reflectivity and diffraction. The morphology and the composition of the interfaces are further characterized by electron microscopy.

Author Index

Bold page numbers indicate presenter