New Horizons in Coatings and Thin Films
Room Pacific D - Session F1-WeA

Nanomaterials and Nanofabrication

Moderators: Diederik Depla, Ghent University, Belgium, **Vladimir Popok**, Aalborg University, Denmark

2:00pm **F1-WeA-1 Polymer Films with Gas-Phase Aggregated Nanoparticles: Formation and Applications***, **Vladimir Popok (vp@mp.aau.dk)**,* Aalborg University, Denmark **INVITED**

In the last couple of decades, nanoparticles (NPs) have been widely used in various research fields and industrial branches. Among many physical and chemical ways of nanoparticle synthesis, the gas-phase aggregation method, also known as cluster beam technique, [1, 2] provides a number of advantages allowing for a very good control of composition because ultra-pure targets are used and the particles are aggregated in vacuum. Formation of not only homo-atomic but alloy and compound NPs with tunable structure and shape (core@shell, Janus- and dumbbell-like, spherical or cubic etc.) is possible. Adjusting the aggregation parameters and adding mass-filtering systems brings a capability of size selection. One more advantage is easy tuning the surface coverage or filling factor of NPs on/in the films. Finally, yet importantly is a capability to form patterned nanostructured films or coatings with gradients of NP surface density.

Polymers are very attractive hosting or supporting media for NPs due to plasticity, flexibility, easy processing, low weight and also low cost. Use of polymers also allows to add required functionality [3, 4]. The talk will overview several most important directions, namely on: (i) tuning resistance of the composite films by controlling the coverage or filling factor of metal NPs and use such materials as elastomeric electrodes, strain gauges and gas sensors; (ii) utilizing localized surface plasmon resonance of NPs to design polymer-based metamaterials with controllable transmittance as well as matrices for enhanced sensing and detection; (iii) polymer coatings with ferromagnetic particles demonstrating excellent absorption of GHz waves as well as tunability of magnetic properties; (iv) utilization of polymer films with NPs as advanced membranes in filtering as well as bactericidal media in food packaging and in medicine.

1. V.N. Popok, E.E.B. Campbell, Rev. Adv. Mater. Sci. 11(1) (2006) 19-45.
2. V.N. Popok, O. Kylian, Appl. Nano 1 (2020) 25-58.
3. V.N. Popok, Cluster Beam Synthesis of Polymer Composites with Nanoparticles, in: Polymer-based Multifunctional Nanocomposites and Their Applications, Eds. K. Song, C. Liu and J.Z. Guo, Elsevier, 2019, 35-76.
4. O. Kylián, V.N. Popok, Frontiers of Nanoscience, 15 (2020) 119-162.

2:40pm **F1-WeA-3 Stress Evolution in Particle Strengthened Metal-Oxide Nanolaminates: Insights from in-Situ Synchrotron Diffraction Experiments***, **Barbara Putz (barbara.putz@unileoben.ac.at)**,* Montanuniversität Leoben, Austria*; A. Sharma,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland*; K. Gradwohl,* Leibniz-Institut für Kristallzüchtung , Germany*; P. Gruber,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM)-WBM, Germany*; D. Többens,* Helmholtz-Zentrum Berlin für Materialien und Energie (HZB), Germany*; X. Maeder, J. Michler,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland

Understanding deformation mechanisms of metal-ceramic nanolaminate coatings (NLC) is crucial in order to exploit their promising mechanical, physical and chemical properties, useful for a wide range of thermal, mechanical and environmental conditions (1). We have fabricated unique, particle strengthened metal/oxide nanolaminates, combining three different deposition techniques: Atomic Layer (ALD), Physical Vapor (PVD) and Nanoparticle (NP) Deposition. Ultrathin oxide layers (<1nm, Al_2O_3) confine the grain growth of metallic PVD films (50nm, Au), for grain sizes distinctly lower than the total film thickness (150nm), improving strength and ductility, while incorporated NPs (W, diameter 4 nm) further enhances mechanical properties. The multilayer microstructures and NP concentrations were confirmed and characterized by cross-sectional transmission electron microscopy (TEM). Stress evolution in the nanocomposites was studied with X-ray diffraction and sin^2psi analysis during in-situ tensile experiments on flexible polymer substrates. Two different nanocomposite geometries (Au/Al_2O_3 and Au + W-NP/Al_2O_3, total thickness 150nm) as well as single Au films (50nm and 150nm) with and without NP reinforcement were investigated to study and isolate the influence of layer thickness and nanoparticle concentration. Results indicate a clear strengthening of 150 nm Au films through multi-layering (Au/Al_2O_3), which can be further increased through the addition of NPs (Au+W-NP/Al_2O_3). Post mortem scanning electron imaging (SEM) of the deformation pattern as well as electrical resistance measurements recorded in-situ during straining indicate that no significant embrittlement was introduced by neither ALD nor NP addition. In summary, the novel manufacturing approach and resulting nanocomposites are promising candidates for multifunctional components in next-generation nano-devices.

(1) A. Misra, J.P. Hirth, R.G. Hoagland, Length-scale-dependent deformation mechanisms in incoherent metallic multilayered composites, Acta Mater. 53 (2005) 4817–4824. https://doi.org/10.1016/j.actamat.2005.06.025.

3:00pm **F1-WeA-4 Structure-Processing Relationships of Chiral Organic-Inorganic Thin Films for Circularly Polarized Light Detection***, **Katherine Burzynski (katherine.burzynski.ctr@afrl.af.mil)**,* AFRL / Azimuth Corp., USA*; E. Muller,* AFRL / UES, USA*; A. Trout,* The Ohio State University, USA*; W. Kennedy,* Air Force Research Laboratory, Materials and Manufacturing Directorate, USA

Photonic quantum information systems (pQIS), optical imaging systems, and analytical spectroscopy tools all benefit from sensitivity to the polarization state of light. Particularly of interest is the detection and discrimination of circularly polarized light (CPL). Currently, the main method to detect CPL requires complex optical systems that cannot easily be incorporated into on-chip circuitry. Direct detection of CPL has been demonstrated by chiral organic semiconductors and metamaterials but suffer from low quantum efficiencies. Chiral organic-inorganic materials are promising for CPL detection due to their ease of fabrication and chiral optoelectronic properties. To date, a limited number of chiral organic metal halide systems possessing intrinsic optoelectronic response to CPL are reported in literature, leaving many chiral systems unexplored. The chiral organic cations, R-(+)- and S-(−)-1-(1-naphtyl)ethylamine (R- and S-NEA+) were incorporated into the lead iodide system. A variety of growth techniques, including spin-coating, confined crystallization, and hydrothermal crystallization, as well as annealing conditions were investigated in an effort to reliably produce functional thin films for CPL photodetection. The fabrication techniques that promote the chiral organic metal halide crystallization and reduce the amount of lead iodide crystallites result in strong chiral optical responses, and ultimately, efficient CPL detection via polarization sensitive photocurrent in thin film devices.

3:20pm **F1-WeA-5 Bio-Inspired Antibacterial Metasurfaces Fabricated by Glancing Angle Deposition***, **Chuang Qu (chuang.qu@louisville.edu)**, J. Rozsa, H. Jung, M. Running, S. McNamara, K. Walsh,* University of Louisville, USA

The goal of this research is to propose an easy and cost-effective fabrication approach of Glancing Angle Deposition (GLAD) for creating antibacterial surfaces, which are inspired by cicada wings. Antibacterial surfaces are known to be applied in a variety of specific interfaces, such as medical implants and food packaging. As Ivanova et al pointed out, bio-inspired surface structuring for antibacterial requires 'further comprehensive and systematic studies'.

This research begins with the examination of the wings of Neotibicen canicularis (an annual cicada in North America, also known as the dog-day cicada, see Fig 1a). Using a scanning electron microscope (SEM), one can observe that the cicada wing is covered nanopillar cone nanostructures, with the tips of the cones sub-100 nm in diameter, and the height of the cones approximately 200 nm (see Fig 1b). The nanopillar cones are semi-hexagonally distributed on the cicada wings with ~170 nm between the neighboring pillars. These antibacterial surfaces compose of appropriately spaced nanopillars cone features, which puncture into bio cells falling on top and keep the surface bacteria-free. Given the nano-level three-dimensional features on the surface of cicada wings, it is extremely difficult to replicate these naturally occurred nanostructures using conventional top-down nanofabrication processes, especially cost-effectively and in large areas. For this reason, we propose to use GLAD combining self-assembly of nanospheres to solve the fabrication problem. GLAD is a versatile bottom-up process that uses physical vapor deposition while maneuvering with incident angle and rotation of the substrate. Although the GLAD approach has been proposed over decades, there is still a lot to discover about this technique, such as the effective seeding rules. This paper will introduce the new seeding rule and scheme for GLAD to replicate the nanopillar cone structures, along with the whole fabrication process using GLAD. Figure 2 presents our initial effort to replicate the cicada wing nanopillar cone structures using GLAD. Finally, gram-negative bacteria (E Coli) are applied on top of the surface for antibacterial testing. Our preliminary results show the effectiveness of the antibacterial property of our synthetic nanostructured film. The proposed GLAD process with the new seeding scheme provides the flexibility in design and optimization of three-dimensional nanofeatures with periodic/random distributions, which allows the further exploring of functional bio-inspired nanostructures.

3:40pm **F1-WeA-6 Polymer Templates-Assisted Design of ZnO Films via Swelling-Assisted Sequential Infiltration Synthesis (SIS) and Swelling Based Infiltration (SBI): Properties, Adsorption Characteristics, and Performance***, **Khalil Omotosho (khalildolapoomotosho@my.unt.edu)**,* University of North Texas, USA

In this paper, we report the properties and adsorption characteristics of ZnO coatings designed with polymer templates-assisted infiltration approaches and their reactions with the environment. For this, we investigated the infiltration of polymer of amphiphilic block copolymer (BCP) templates with ZnO by comparison of 2 infiltration approaches, the swelling-assisted sequential infiltration synthesis (SIS) and the swelling-based infiltration (SBI), followed by polymer templates removal by oxidative thermal annealing for the design of porous ZnO films. Using the quartz crystal microbalance (QCM), we compared the infiltration efficiency of both methods. The XRD and XPS data revealed that the SBI-based porous ZnO films have a more disordered structure with a high surface concentration of OH groups, leading to a more hydrophilic film. We monitored the chemical interactions of the polymer templates before and after infiltration using the FTIR. Our results indicate that the performance of the ZnO coatings is highly dependent on the infiltration approach adopted, the templates, and their interactions with organic molecules. These results suggest new ways to efficiently design highly porous metal oxide coatings that can be adapted for various applications.

4:00pm **F1-WeA-7 Pulsed Aerosol Assisted Plasma Deposition: Process and Film Composition Characterization Using Nanoparticles Optical Properties***, **Adèle Girardeau (adele.girardeau@laplace.univ-tlse.fr)**,* LAPLACE, LCC, Safran Tech, France*; G. Carnide,* LAPLACE, LCC, IMRCP, France*; A. Mingotaud,* IMRCP, France*; M. Cavarroc,* Safran Tech, France*; M. Kahn,* LCC, France*; R. Clergereaux,* LAPLACE, France

Aerosol-assisted processes enable to deposit thin films, homogeneous[1,2] or nanocomposite[3–6]. For example, the nebulization of colloidal solutions, i.e. liquid solutions containing nanoparticles, in plasma processes have been widely used for nanocomposite thin film deposition. In this work, an alternative method, called direct liquid reactor-injector (DLRI) of nanoparticles, is applied. It allows to synthesize nanoparticles prior to their injection in the plasma in a pulsed injection regime[7].

In a low-pressure RF plasma coupled with DLRI of ZnO nanoparticles, it enables to form nanocomposite thin films with really small (<10 nm in diameter) and highly dispersed nanoparticles embedded in a matrix[7] that exhibits the classical optical properties of ZnO (absorbance at their band-gap - 3.37 eV and fluorescence when illuminated by ultraviolet light - 320-360 nm[8–10]). However, the volume fraction of nanoparticles embedded in the matrix is 5 times lower than expected. Indeed, in-situ optical emission spectroscopy (OES) of the plasma presents the characteristic luminescence of ZnO nanoparticles suggesting that nanoparticles are efficiently confined in the plasma volume during the process and does not participate to the nanocomposite formation.

To estimate the number of nanoparticles confined in the plasma volume and the global process balance of matter, one must establish the relation between the absorption / fluorescence and the number of nanoparticles. Here, we report an abacus obtained with ZnO nanoparticles synthesized by an organometallic approach: it shows that the optical characteristics of the ZnO nanoparticles follow the classical Beer-Lambert and luminescence laws, a useful tool for in-situ analyses. It also enables to determine the absorptivity and the quantum yield of the ZnO nanoparticles produced.

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