Functional Thin Films and Surfaces
Room Town & Country B - Session MB3-2-ThA

Nanomaterial-based Thin Films and Structures II

Moderators: Ondrej Kylian, Charles University, Prague, Czechia, **Vladimir Popok**, Aalborg University, Denmark

2:40pm **MB3-2-ThA-5 AFM-SEM Imaging for TEM Grid Mounted Nanomaterials***, **Kerim Arat (kerim.arat@qdusa.com)**, S. Spagna,* Quantum Design Inc., USA

Microscopists employing Transmission Electron Microscopy (TEM) alongside TEM-based Energy Electron Loss Spectroscopy (EELS) to study the properties of nano-materials often need to assess physical parameters like heights and cross-sectional shapes of the samples under examination. Due to the typical sub-five nanometer thickness of membranes in TEM grids, conducting Atomic Force Microscopy (AFM) measurements on grid-mounted samples is currently arduous and time-intensive. This paper introduces a fully integrated AFM and Scanning Electron Microscope (SEM) correlative workstation, facilitating direct sample imaging on a TEM grid using both techniques. This seamlessly integrated and user-friendly AFM-SEM microscopy workstation unlocks unparalleled measurement capabilities at the nanoscale, particularly for complex geometries. The AFM-SEM imaging of TEM grid-mounted samples streamlines measurement workflows, leading to enhanced data output rates. Additionally, the platform supports easy expansion of functionalities, such as elemental analysis through Energy Dispersive X-ray Spectroscopy (EDS). The diverse array of AFM modes available (including Contact, Tapping, Off-resonance, Conductive, Magnetic, and Electrostatic) enables the extraction of various physical properties from the sample.

3:00pm **MB3-2-ThA-6 Sputtering onto Liquids: Towards the Synthesis of Ultra-Fine Nanoparticles***, H. Lasfargues, L. Freymann, S. Shankar, M. Momma, T. Schneider, **Clio Azina (azina@mch.rwth-aachen.de)**,* RWTH Aachen University, Germany

Physical vapour deposition approaches are highly versatile techniques which allow the deposition of a variety of material systems typically under thin film form. While thin films are the most common outcome of vapour-based deposition methods, nano-objects, such as nanoparticles, can also be produced by switching conventional solid substrates with liquid ones. Herein, the concept of sputtering onto liquids will be introduced. SoL is a technique which allows the synthesis of ultra-fine (<10 nm) nanoparticles in a vacuum-compatible liquid. While this approach has existed for more than 50 years, the mechanisms of nanoparticle formation are still not fully described. In fact, the effect of the plasma on the synthesis and stability of the suspensions is rarely discussed in the literature. Herein, we will attempt to identify the effects of the sputtered atoms kinetic energy and flux on the size of Ag nanoparticles sputtered onto polyethylene glycol and castor oil. From the systematic study it is shown that the flux and kinetic energy of the sputtered atoms have a combined effect on the nanoparticle size distribution. In addition, the functional groups of the liquids also impact the growth by stabilizing the incoming species despite their potentially elevated kinetic energies.

3:20pm **MB3-2-ThA-7 Superhard Hexagonal Tib$_2$/Hf Single Crystal Superlattices for Toughness Enhancement***, **Naureen Ghafoor (naureen.ghafoor@liu.se)**,* Linköping University, Sweden*; N. Koutná, S. Lin,* TU Wien, Austria*; F. Angáy, M. Lorentzon, F. Eriksson, L. Hultman, J. Birch,* Linköping University, Sweden

We present combined experimental and theoretical investigations on iso-structural TiB_2/Hf superlattices, demonstrating the impact of individual layer thicknesses on the hardness and toughness.*Ab initio* calculations suggest that hexagonal alpha-structured TiB_2 and hexagonal close-packed Hf exhibit a basal-plane lattice and shear modulus mismatch of 0.16 Å (5.4%) and 200 GPa, respectively, hence providing a basis for hindering dislocation glide across interfaces. Superlattices are deposited using ion-assisted magnetron sputter deposition, designed with a modulation period of 5 nm (to allow for theoretical modeling of the structure), where the individual layer thicknesses range from 1 to 4 nm, as analyzed by XTEM, XRD, ERDA, and XPS. Superhard single crystal TiB_2/HfB_2 diboride superlattices with 40 GPa nanoindentation hardness form at lower Hf thicknesses and at high growth temperatures. Furthermore, structural characterization reveals boron diffusion from overstoichiometric TiB_2 into Hf layers, resulting in single crystal TiB2 and understoichiometric HfB_2, in response to the high negative enthalpy of Hf-B. Thanks to self-diffusion, no strain build-up and epitaxial breakdown of superlattice layers are observed in films with period numbers as high as 375. We show that for achieving TiB_2/Hf superlattice, it is critical to reduce boron diffusion by controlling the TiB_2 stoichiometry. Consequently, nanoindentation combined with microcantilever bending testing will be presented in relation to structural and mechanical predictions by *ab initio* calculations as well as machine-learning-potential molecular dynamics, where the latter uses a moment-tensor-type potential developed and carefully validated for the purpose of this study.

4:00pm **MB3-2-ThA-9 Study on Improving the Performance of Zinc Oxide Piezoelectric Pressure Sensor by Doping Vanadium***, **Heng-Chi Chu (juliachu2000@gmail.com)**, S. Brahma, J. Huang,* National Cheng Kung University (NCKU), Taiwan

Piezoelectric effect is a phenomenon in which positive and negative ions are displaced generating electric polarization with the application of stress on the materials having non-centrosymmetric crystal structure. Zinc oxide possesses both piezoelectric and semiconductor properties. The applied pressure generates piezo-potential thereby creating a Schottky barrier at the interface of the semiconductor and the metal electrode that can be modulated by the variation of the strain. This characteristic can be applied to fabricate the piezoelectric pressure sensors devices based on ZnO/doped ZnO and investigate the stress sensitivity. However, the low piezoelectric coefficient (12.4 pC/N) of ZnO restricts further development zinc oxide based piezoelectric devices. Consequently, we doped zinc oxide with vanadium and doping of smaller ionic radius vanadium at the zinc sites enhanced electric polarization and improved the piezoelectric coefficient. Furthermore, vanadium doping induced changes in the grain size and energy band structure and influenced the performance of the piezotronic effect. We employed radio frequency magnetron co-sputtering to deposit V doped ZnO thin films by using zinc oxide and vanadium pentoxide as targets and V doping concentration was controlled by the variation of the working power of vanadium pentoxide target. Subsequently, we fabricated a pressure sensor by depositing gold electrodes to create a Schottky barrier and investigated the piezoelectric stress sensitivity. SEM results revealed that vanadium doping led to the grain size reduction. XPS analysis of the oxygen spectrum indicated that doping led to surface adsorbates and an increase in intrinsic defects. The XPS spectra of vanadium showed the presence of both V^{5+} (V^{3+}) ions at low (high) V doping concentrations. As the doping concentration increased, the proportion of V^{5+} decreased due to the redox effects, shifting to V^{3+} with a larger radius. This trend aligns with the piezoelectric coefficient. UV-vis and UPS analyses provided insights into the energy band structure. Vanadium doping shifted the Fermi level towards the conduction band, resulting in a smaller work function and band gap compared to undoped zinc oxide. This induced a more stable Schottky barrier and improved carrier transport mechanism. In the piezoelectric stress sensitivity test, vanadium doping effectively enhanced current and stress sensitivity. However, higher doping concentration decreased the sensitivity due to the lower piezoelectric coefficient. In summary, our research aims to combine the above analyses to identify optimal sputtering parameters, thereby enhancing the performance of piezoelectric pressure sensors.

4:20pm **MB3-2-ThA-10 Glancing Deposited Wide Band Gap Zirconia Nanohelical Metamaterial Platforms:Unveiling Broad-Band UV-Active Chirality***, **Ufuk Kilic (ufukkilic@unl.edu)**,* University of Nebraska - Lincoln, USA*; M. Hilfiker,* Onto Innovation Inc., USA*; S. Wimer,* University of Nebraska - Lincoln, USA*; C. Argyropoulos,* Pennsylvania State University, USA*; E. Schubert, M. Schubert,* University of Nebraska - Lincoln, USA

Chirality is a property of asymmetry in molecules or objects that cannot be superimposed onto their mirror images. This symmetry breaking phenomenon is fundamental to various fields such as chemistry, biology, physics, and materials science. Optical manifestation of chirality known as circular dichroism is the differential absorption response of the object to the incoming left- and right- handed circularly polarized light. However, chirality found in nature is very weak, almost impossible to spectrally control, and mostly emerges in the vacuum ultraviolet (VUV) part of the spectrum [1]. Utilizing metamaterial platforms to boost chirality and to detect these chiral molecules presents challenges, as many are designed for the operation in the infrared (IR) to the visible spectral range [1,2]. The utilization of ultra-wide band gap metal oxides in nanostructure fabrication has received limited attention in the literature, particularly concerning their chiral properties [2]. In this study, we explored the fabrication of zirconia (ZrO_2) thin films using electron beam evaporated glancing angle deposition (GLAD) technique. This recently emerging bottom-up fabrication technique is known for its capacity to produce various 3D nano-morphologies over wafer-scale area.

Leveraging the substrate manipulation arm, the normal incidence of the particle flux onto the surface leads to the fabrication of flat, uniform, thin films of ZrO_2. Through generalized spectroscopic ellipsometry (GSE) technique, we extracted the frequency dependent complex dielectric function and performed critical point model dielectric function analysis to identify the band-to-band transitions within near-IR to VUV spectral range. On the other hand, impinging the particle flux on the sample substrate at extremely oblique angle (85.5°) together with continuous rotation of sample (24 sec/rev) permits the fabrication spatially coherent, well-oriented nano-helices. Hence, we experimentally detected VUV-active strong circular dichroism responses from ZrO_2 nano-helical metamaterials using the Mueller matrix GSE technique. Furthermore, we employed finite element modeling (FEM) to theoretically verify these responses and observed that the chiral response can be tailored in terms of magnitude and spectral position using structural parameters of nano-helices. Furthermore, we envision a potential use of these chiral metamaterials in areas which include high power required chiroptic photonic/electric circuit designs, UV active topological insulators, chiral sensor technologies.

References:

[1] Kilic U. et al., Adv. Funct. Mater. 31.20: 2010329,(2021).
[2] Sarkar, S. et al., Nano letters 19.11: 8089-8096,(2019).

Author Index

Bold page numbers indicate presenter