Thin Films
Room 317 - Session TF2-MoA

Fundamentals of TF I

Moderators: Joe Becker, Kurt J. Lesker Company, **Tania Sandoval**, Universidad Técnica Federico Santa María

3:45pm **TF2-MoA-10 Optimization and Stabilization of Stress in SiO_x for Piezoelectric Thin Films Stress Compensation**, ***J Goodman***, *Burcu Dursun,* The Pennsylvania State University*; Gavin Frueh, Kenneth Buffo, Casey DeRoo,* The University of Iowa*; Paul Reid,* Harvard & Smithsonian Center for Astrophysics*; Hanyuan Liang, Thomas Jackson, Susan Trolier-McKinstry,* The Pennsylvania State University

Lead zirconate titanate (PZT) thin films on Si substrates experience tensile stress due to the difference in thermal expansion coefficients between Si (2.3–4.5 × 10^{-6}/K) and PZT (5.5–8.0 × 10^{-6}/K)[1,2]. Stress in the PZT films and their electrode stacks leads both to deformation of the substrate, and to lower piezoelectric coefficients due to suppressed domain wall motion[2]. One method being investigated to counteract this tensile stress is the use of a compressive compensation layer. SiO_x thin films are being investigated for this application as the compressive stress generated by SiOx films can be tailored as a function of sputtering pressure[3]. Thus, depositions can be adjusted to compensate for substrate distortion generated by the PZT films and their electrode stacks during fabrication. The goal of this work is to characterize the magnitude and stability of the stress generated during SiO_x deposition.

For this work, SiO_x films were deposited onto Si wafers using radio frequency magnetron sputtering at chamber pressures between 2.5 and 3.0 mTorr. The thicknesses of the SiO_x films ranged from 180 to 1220 nm, with the indexes falling between 1.60 and 1.90. The high refractive index relative to SiO_2 (1.46)[4] indicates that the deposited films are oxygen deficient.

The compressive stress generated was between 330 and 490 MPa immediately following deposition, which is sufficient to compensate for the expected stress in the actuator stack (180±20 MPa/μm).

However, the compressive stress in the deposited SiO_x layers decreased over a seven-month period, dropping by >90 MPa in some cases. This decrease in compressive stress over time can be stabilized through growth of an Al2O3 barrier layer immediately following SiO_x deposition. Films covered in Al_2O_3 had a smaller change in stress, <±5 MPa, over the same period. The Al_2O_3 layers for this work were grown using atomic layer deposition at 200˚C with Trimethylaluminum (TMA) and H_2O precursors. Work on characterizing the generation and degradation of stress created by SiO_x will be reported, as well as work on stabilizing the stress state with an Al_2O_3 passivation layer.

References:

1. G. Han, et al. J. Appl. Phys. 2011; 110 (12): 124101. https://doi.org/10.1063/1.3669384

2. K. Coleman, et al. J. Appl. Phys. 2019; 126 (3): 034101. https://doi.org/10.1063/1.5095765

3. S. Chandra, et al. Sādhanā. 2009. 34, 543–556 (2009). https://doi.org/10.1007/s12046-009-0032-y

4. W. A. Pliskin, et al. J. Appl. Phys. 1965; 36(6): 2011–2013. https://doi.org/10.1063/1.1714393

4:00pm **TF2-MoA-11 The Origins of Mxene Optical Properties**, ***Zahra Fakhraai,*** University of Pennsylvania **INVITED**

The functional properties of most 2D materials are well defined by their chemical composition. In contrast, for metal-organic complexes, the organic ligand can play a key role in controlling the electronic band structure of the complex. In this presentation, I will discuss the optical properties of MXenes, a relatively new class of highly conductive two-dimensional materials. MXenes are 2D transition metal carbides that are typically made by etching of a 3D crystal. In the prototypical $Ti_3C_2T_x$ MXenes, the termination state depends on the synthesis, etching, and delamination processes, which together result in mixed terminations consisting of =O, -OH, -F, and/or -Cl groups. In addition to being metallic, $Ti_3C_2T_x$ MXenes also show a broad near-infrared (IR) optical extinction (~1.5 eV), which has been widely attributed to a localized surface plasmon resonance (LSPR). However, using experimental measurements and density functional theory (DFT) calculations, we demonstrate that in mixed-terminated $Ti_3C_2T_x$ MXenes, this low-energy band is an interband transition specifically arising from oxygen-terminated ($Ti_3C_2O_2$) MXene. As such, we establish that in addition to the chemical structure, post-synthetic variations in MXene terminating groups can dramatically alter their band structure and optical properties. For example, we show that in $Ti_3C_2Cl_2$, where -Cl is the predominant termination, the low-energy transition vanishes, resulting in strongly metallic properties. In thin films, this property change can lead to the design of novel optical properties, such as hyperbolicity, while engineering the band structure can produce transparent optical regions in the IR spectral range. These variations in band structure due to termination states could play a significant role in the light-matter interactions in MXenes, result in electron-phonon coupling effects, and affect their thermal stability at high temperatures.

4:30pm **TF2-MoA-13 Optical and Structural Properties of Ga_2O_3 Thin Films Deposited by Reactive and Non-Reactive Sputtering**, ***Marcell Gajdics,*** *Ildikó Cora, Dániel Zámbó, Zsolt Horváth Endre, Béla Pécz,* HUN-REN Centre for Energy Research, Hungary

The ultrawide bandgap semiconductor, Ga_2O_3 has numerous potential applications in the fields of optoelectronics and high-power electronics. Gallium oxide thin films can be grown by a variety of methods, among which radio frequency sputtering is a commonly used technique, as it allows highly uniform layers to be deposited at low temperatures. In most cases, a ceramic Ga_2O_3 target is used for the sputter deposition of Ga_2O_3. In our work, we present an alternative method, i.e. reactive sputtering of a liquid Ga target. We have shown that by using this technique, layers close to the ideal stoichiometry can be deposited with higher deposition rate than by using a Ga_2O_3 target. The optical properties (e.g. refractive index) were studied as a function of the oxygen concentration in the films. Post-deposition heat treatments were also performed on the amorphous as-deposited layers to study the annealing-induced structural and optical changes. The crystallization and phase evolution were investigated by X-ray diffraction and transmission electron microscopy; in the latter case, both ex situ and in situ measurements were performed. It was found that the crystallization of Ga_2O_3 occurs in two steps: in the first step, the formation of the metastable γ-Ga_2O_3 phase was observed, and then, as a result of further annealing, the thermodynamically stable β-Ga_2O_3 appears. The photoluminescence emission and the optical bandgap were also measured at different annealing temperatures, and the results were correlated with the structural properties. The two crystalline phases have distinct emission spectra, and the photoluminescence of the β-Ga_2O_3 is also shown to depend on the annealing atmosphere.

5:00pm **TF2-MoA-15 Plasma-Driven Microstructural Evolution in TaC Thin Films Deposited by DC, RF, and HiPIMS Sputtering**, ***Tainara Coutinho de Carvalho***, *Jon-Paul Maria,* Penn State University

Controlling the microstructure of TaC thin films is essential for applications requiring high hardness, thermal stability, and chemical inertness, where functional performance is strongly governed by growth kinetics during deposition. Although DC, RF, and HiPIMS sputtering generate plasmas with distinct and well-known energetics, their comparative influence on TaC microstructural evolution under equivalent deposition rates remains insufficiently understood.

In this work, TaC films were deposited by DC, RF, and HiPIMS magnetron sputtering while systematically varying methane flow, working pressure, substrate temperature, target-to-substrate distance, deposition power, and film thickness. Structural and microstructural characterization was performed by XRD and SEM for all films, with TEM investigations on representative samples to understand microstructure at finer length scales.

Phase formation showed strong sensitivity to methane availability, with cubic TaC predominating under most conditions and Ta_2C forming only at low methane flow during RF deposition, suggesting that limited reactive carbon supply under RF plasma conditions favors the formation of metal-rich carbide phases. Despite comparable deposition rates, each sputtering mode produced distinct grain morphologies, highlighting the strong influence of plasma energetics and species transport on growth pathways. DC deposition promoted faceted grains within a narrow methane range, RF induced a transition from elongated Ta_2C grains to triangular TaC grains, and HiPIMS stabilized triangular morphologies across a broader methane window, adding a kick pulse to HiPIMS growth progressively suppressed this anisotropic growth behavior. Total pressure and target-to-substrate distance produced distinct morphological responses in DC and HiPIMS

films, reflecting differences in collisional transport and arrival energy of the depositing species, whereas substrate temperature produced comparatively limited effects.

Changes in deposition power and film thickness revealed that these morphological transitions are associated with shifts in the balance between nucleation density and competitive grain growth. Ultimately, this work highlights how plasma-driven growth kinetics can be leveraged to design carbide thin films with tunable and application-specific microstructures.

5:15pm **TF2-MoA-16 Interfacial Engineering of Battery Materials using Atomic Layer Deposition*, Neil Dasgupta,*** University of Michigan, Ann Arbor **INVITED**

Interfaces and interphases play a critical role in battery performance, both in current state-of-the-art Li-ion batteries (LIBs), as well as next generation battery technologies. Therefore, there are great efforts to understand, control, and improve the properties of battery interfaces and interphases. This quickly becomes a multi-dimensional optimization problem, where the required properties of interfaces span from performance (i.e. fast rate capability), stability (i.e. long calendar life) and compatibility with the adjacent chemical and material phases. To address these challenges, there has been increasing interest in the application of 'artificial interphase' layers, which are typically comprised of nanoscale thin-film coatings along electrode-electrolyte interfaces. From a manufacturing perspective, it is critical that these surface coatings be deposited in a conformal, reproducible, scalable, and low-cost manner.

Towards these goals, our research group has developed a range of surface coating layers for battery applications, both for LIBs with liquid electrolytes, as well as next-generation systems such as Li metal anodes and solid-state batteries. In this talk, I will summarize recent progress towards precise and tunable interfacial control in batteries with both liquid and solid electrolytes, using atomic layer deposition (ALD) as an enabling platform. I will describe the development of advanced ALD chemistries, beyond the binary oxide systems that are typically employed. In LIBs, I will describe how surface coatings can simultaneously enable low-temperature and fast charging of graphite anodes without Li plating. In solid-state battery systems, I will describe the stabilization of cathode/solid electrolyte interfaces, enabling high-voltage cycling above 4.5 V. Finally, I will describe our efforts towards scalable manufacturing of ALD-coated battery electrodes, through the development of atmospheric-pressure spatial ALD technologies.

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