

Thin Films

Room 115 - Session TF1-TuM

Thin Films: Controlling Crystalline Phases

Moderators: Lauren Garten, Georgia Institute of Technology, April Jewell, Jet Propulsion Laboratory

8:00am **TF1-TuM-1 Peter Mark Memorial Award Talk: Strain-Induced Magnetism and Superconductivity in Single-Crystalline Heusler Membranes, Jason Kawasaki¹**, University of Wisconsin - Madison **INVITED** Single-crystalline membranes of functional materials enable the tuning of properties via extreme strain states; however, conventional routes for producing membranes require the use of sacrificial layers and chemical etchants, which can both damage the membrane and limit the ability to make them ultrathin. I will describe how the growth of thin films on graphene-terminated substrates enables synthesis of single crystalline, mechanically exfoliatable membranes [1,2]. Using rippled membranes of the Heusler compound GdPtSb, we demonstrate the first experimental example of flexomagnetism, that is, ferro/ferri-magnetism induced by strain gradients [3]. I will also describe evidence of superconductivity induced in another Heusler membrane via strain. More broadly, Heusler membranes provide highly tunable platform for tuning ferroic order, topological states, and correlations [4].

[1] S. Manzo, et. al., *Nature Commun.*, 13, 4014 (2022). <https://doi.org/10.1038/s41467-022-31610-y>

[2] D. Du et. al., *Nano Lett.* 22, 21, 8647 (2022). <https://doi.org/10.1021/acs.nanolett.2c03187>

[3] D. Du, et. al., *Nature Commun.*, 12, 2494 (2021). <https://doi.org/10.1038/s41467-021-22784-y>

[4] D. Du, et. al. *APL*, 122, 170501 (2023). <https://doi.org/10.1063/5.0146553>

8:30am **TF1-TuM-3 Stabilization of P63cm ScFeO₃ on (111) Pt Mediated via an Fe₃O₄ Interlayer, Marshall Frye, J. Chin**, Georgia Institute of Technology; *N. Parker, M. Barone*, Cornell University; *L. Garten*, Georgia Institute of Technology

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Ferroelectric photovoltaics are an emerging renewable energy technology where charge separation occurs in a single layer and the open-circuit voltage can be larger than the bandgap. The metastable *P6₃cm* phase of ScFeO₃ (h-ScFeO₃) is an ideal candidate for ferroelectric photovoltaics due to its polar crystal structure and narrow bandgap (1.2 eV). While h-ScFeO₃ can be grown on Al₂O₃ using a layered approach,¹ on conductive substrates, such as (111) Pt, only the ground state bixbyite phase of ScFeO₃ is stable. h-ScFeO₃ growth on a substrate with high conductivity and low epitaxial strain is critically needed for photovoltaic device fabrication.

In this work we grew h-ScFeO₃ on (111) platinum via molecular beam epitaxy (MBE). The stabilization of the h-ScFeO₃ phase was enabled by an Fe₃O₄ interlayer. This approach is adapted from reports of growth of hexagonal LuFeO₃ on oriented Fe₃O₄ via MBE.² Epitaxial (111) Pt which was deposited on c-Al₂O₃ was found to have a narrow (~0.005°) full width at half maximum (FWHM) rocking curve about the (111) peak, indicating a highly crystalline film. After depositing (111) Pt, a Fe₃O₄ layer was deposited. ScFeO₃ was then deposited on the Fe₃O₄ film with alternating depositions of Sc and Fe.¹ The films are solely (0002̄) oriented of h-ScFeO₃ with clear Laue oscillations. Furthermore, rocking curves about the (0004) hexagonal ScFeO₃ peak have a FWHM of 0.07°, indicating a highly crystalline film. Films grown on conductive substrates then enabled measurements of the carrier mobility and dielectric response of the h-ScFeO₃. Overcoming the challenge of growing h-ScFeO₃ on conductive substrates will allow us to

utilize these materials advantageous properties for high-efficiency photovoltaics.

1. Garten, L. M. et al. Stromataxic Stabilization of a Metastable Layered ScFeO₃ Polymorph. *Chem. Mater.* **33**, 7423–7431 (2021).
1. Zhang, X. et al. Effect of interface on epitaxy and magnetism in h-RFeO₃/Fe₃O₄/Al₂O₃ films (R = Lu, Yb). *J. Phys. Condens. Matter* **29**, 164001 (2017).

8:45am **TF1-TuM-4 Thermo-Controlled Defect Engineering in Ceria: An XPS and Raman Spectroscopy Study with In-Situ Heating, U. Kumar, C. Feit, J. Prakash Ganesan, S. Berriel, Y. Fu, C. Neal, E. Kolanthai, P. Banerjee, Sudipta Seal**, University of Central Florida

Cerium oxide nanostructures possess unique oxidative recycling properties, enabling their use in various engineering applications. However, predictable and precise defect engineering remains challenging. Ceria thin films offer a method to engineer defects by controlling thickness, albeit with limitations. To further enhance performance, we fabricated 2.9 nm and 0.5 nm CeO₂-33 nm VO₂ bilayers using atomic layer deposition (ALD), leveraging the low-temperature phase transition of VO₂. We established a test vehicle utilizing X-ray Photoelectron Spectroscopy (XPS) with in-situ heating and cooling to study defect levels. The Ce³⁺/Ce⁴⁺ ratio was determined using Ce3d XPS scans during heating and cooling. A remarkable Ce³⁺/Ce⁴⁺ ratio of 5.97 (Ce³⁺ ~ 85%) was obtained and modulated over a temperature range from room temperature to 90 Å°C. Additionally, Raman studies with in-situ heating and cooling were conducted to understand the mechanism behind this phenomenon.

9:00am **TF1-TuM-5 Hybrid Pulsed Laser Deposition Growth of Epitaxial Chalcogenides, Mythili Surendran**, USC

Chalcogenides such as transition metal dichalcogenides (TMDC) and chalcogenide perovskites (CP) have garnered attention for their electronic and photonic properties. Despite their promising potential for electronic applications, the epitaxial growth of these materials is still in its nascent stages. Adding to the complexity, a most of the emerging chalcogenides are vapor pressure mismatched transition metal compounds. The stark differences in vapor pressures between transition metal cations and chalcogen anions present a great challenge during epitaxial growth. This challenge is particularly pronounced in sulfide thin film growth and exacerbated in CPs due to their complex stoichiometries. Addressing these complexities demands innovative strategies to achieve precise flux control and maintain stoichiometric integrity during epitaxial growth.

Sulfides have been mostly grown using CVD, although MBE, MOCVD, pulsed laser deposition (PLD) and several other techniques have been exploited. However, large area and high-quality growth with precise and uniform thickness control and low defect densities still remain a challenge due to a large cation-sulfur vapor pressure mismatch, corrosive and reactive nature of most chalcogen precursors, high synthesis temperatures and the propensity to oxidize easily in the presence of oxygen at these high temperatures. Most growth techniques utilize H₂S as the sulfur source. However, H₂S is a toxic, hazardous, and flammable gas and require high temperatures for efficient decomposition and sulfurization, resulting in high defect densities.

Here, we discuss epitaxial growth of CPs and TMDCs (specifically sulfides) using a novel hybrid PLD (*Adv. Mater* 2024) approach wherein we employed organo-sulfur precursors as the sulfur source. Large area epitaxial thin films of Group IV 2D chalcogenides such as TiS₂ (metallic) and ZrS₂ (semiconducting) and CPs such as BaZrS₃ and BaTiS₃ were successfully grown. This novel method utilizes precursors with optimum vapor pressures and they decompose at a lower temperatures (~250-400°C) to provide dissociated sulfur species. Structural and electrical characterization, along with low temperature transport studies reveal low defect densities and high carrier mobilities in these films. This work emphasizes on low temperature growth of high mobility refractory metal-based sulfides, especially with BEOL compatibility. Although slightly elevated temperatures were required for CPs, the interfacial roughness and optoelectronic performance were improved. The potential of these chalcogenides as candidates for transparent and conducting layers in chalcogenide-based optoelectronic devices will be discussed.

9:15am **TF1-TuM-6 Atomic Layer Deposition of Entropy Stabilized Zr_xTa_yO_z, Shane Witsell, J. Haglund, J. Conley**, Oregon State University

High entropy oxides (HEOs) can exhibit enhanced mechanical, refractory, catalytic, cryogenic, and dielectric properties over conventional materials [1]. The classic understanding of HEOs is founded on a high degree of

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configurational disorder as well as a positive enthalpy of formation. It has been thought that five discrete elements were necessary to cause this high degree of disorder ($S_{\text{config}} > 1.6R, J/\text{mol}\cdot\text{K}$). However, it has recently been shown that $A_6B_2O_{17}$ perovskites, where $A = \text{Zr}$ or Hf and $B = \text{Nb}$ or Ta can demonstrate an exceptionally high degree of disorder (S_{config} of 4.50R, $J/\text{mol}\cdot\text{K}$) [2]. Though these materials have been synthesized by powder sintering [5] and ternary ZrTaO has been demonstrated with atomic layer deposition (ALD) [3], entropy stabilized $\text{Zr}_x\text{Ta}_y\text{O}_z$ has yet to be achieved via ALD. Herein we report the successful transformation of ALD $\text{Zr}_x\text{Ta}_y\text{O}_z$ into the entropy-stabilized form.

ZrO_2 and Ta_2O_5 were synthesized via ALD using tantalum ethoxide ($\text{Ta}(\text{OEt})_5$) and zirconium chloride (ZrCl_4), respectively, with O_3 [3]. $\text{Zr}_x\text{Ta}_y\text{O}_z$ was deposited using modulated $\text{ZrCl}_4/\text{N}_2/\text{Ta}(\text{OEt})_5/\text{N}_2/\text{O}_3/\text{N}_2$ super cycles [4]. Films were deposited on Si substrates and were amorphous as-deposited. Following annealing at 800°C for 30 minutes in N_2 , x-ray diffractometry (XRD) spectra (Fig. 1) show a strong overlap between annealed ALD $\text{Zr}_6\text{Ta}_2\text{O}_{17}$ and the expected peaks for HEO stabilized $A_6B_2O_{17}$ [5], and no overlap with binary ZrO_2 or Ta_2O_5 .

Metal/insulator/Si (MIS) electrical devices were fabricated using Ag top electrodes. 800 °C annealed entropy stabilized $\text{Zr}_x\text{Ta}_y\text{O}_z$ devices exhibited unipolar threshold voltage switching when illuminated, with a ON/OFF current ratio of 7×10^3 and a $\sim +0.56$ MV/cm SET voltage. Switching did not occur in the dark. Unannealed amorphous $\text{Zr}_x\text{Ta}_y\text{O}_z$ devices did not exhibit switching in this voltage range but required a +1.8 MV/cm SET voltage and had an ON/OFF ratio of only $\sim 10^2$. Switching under illumination is still under investigation and was possibly due to the formation of oxygen vacancies in the entropy stabilized matrix as opposed to the un-annealed amorphous form [6].

1. Aamlid, S. *et al.* *J. Am. Chem. Soc.* **145** (2023).
2. Voskanyan, A. *et al.* *Scripta Materiala* **204** (2021).
3. Kukli, K. *et al.* *AIP Advances* **7** (2017).
4. Nguyen, C. *et al.* *Chem. Mater.* **33** (2021).
5. Spurling, R. *et al.* *J. Mater. Sci* **85** (2023).
6. Li, H. *et al.* *Coatings* **11** (2021)

9:30am TF1-TuM-7 Stabilizing Oriented Barium Nickelate Thin Films, Ian Graham, M. Frye, L. Garten, Georgia Institute of Technology

Oxygen evolution reaction (OER) is the rate limiting step inhibiting the production of fuel from water.^{1,2} Barium nickelate (BaNiO_3) is a potential candidate for OER catalysis because it has an order of magnitude higher catalytic activity for the OER compared to the current benchmark iridium oxide (IrO_2).¹ Understanding the impact of crystallographic orientation and oxygen vacancy concentration on OER catalytic activity is critical to enabling BaNiO_3 catalysts.^{1,2}

In this work, we demonstrate the growth of oriented BaNiO_3 films via pulsed laser deposition (PLD). Films were deposited from a $\text{BaNiO}_{2.36}$ target onto (0001) Al_2O_3 substrates over a range of deposition temperatures, laser fluences, and oxygen partial pressures. X-ray diffraction shows that the orientation of BaNiO_3 is dependent on the deposition temperature. The (11-20) orientation of BaNiO_3 grows at temperatures below 500 °C, whereas increasing the deposition temperature from 400 °C to 500 °C leads to (10-10) BaNiO_3 . Further increasing the deposition temperature to 700 °C changes the orientation of the film to predominately (0002) oriented. X-ray photoelectron spectroscopy shows the oxidation state of films deposited under different deposition oxygen partial pressures. Reducing deposition $p\text{O}_2$ from 1.65×10^{-2} mbar to 1.27×10^{-2} mbar shows a 4% decrease in oxygen atomic percentage. Atomic force microscopy shows that decreasing the laser fluence and oxygen partial pressure decreases the root mean square surface roughness of the deposited films. Reducing the laser fluence from $3.5 \text{ J}/\text{cm}^2$ to $2.5 \text{ J}/\text{cm}^2$ shows a 3 nm decrease in the root mean square surface roughness, while decreasing the oxygen partial pressure from 9.1×10^{-2} mbar to 1.65×10^{-2} mbar shows a 1 nm decrease in root mean square surface roughness. Co-planar top electrodes enabled impedance spectroscopy and dielectric measurements. Impedance data shows the migration of oxygen vacancies which play an important role in OER. Elucidating the impact of crystallographic orientation on oxygen vacancy migration gives insight into how crystallographic orientation affects OER catalytic activity.

References

1. Lee, J. G. *et al.* A New Family of Perovskite Catalysts for Oxygen-Evolution Reaction in Alkaline Media: BaNiO_3 and $\text{BaNi}_{0.83}\text{O}_{2.5}$. *J. Am. Chem. Soc.* **138**, 3541–3547 (2016).

2. Plevová, M., Hnát, J. & Bouzek, K. Electrocatalysts for the oxygen evolution reaction in alkaline and neutral media. A comparative review. *Journal of Power Sources* **507**, 230072 (2021).

9:45am TF1-TuM-8 Optimizing Sputter Deposition of Bi_2Te_3 and Sb_2Te_3 for Photolithographic Device Fabrication, Rumana Zahir, University of Central Florida; F. Gonzalez, Truventic LLC; D. Smalley, A. Bharath, E. Nino, K. Sundaram, M. Ishigami, R. Peale, University of Central Florida

Antenna-coupled thermoelectric junctions have potential for THz and mm-wave detection and energy harvesting. These require patterned deposition of thermoelectric materials with a junction at the feed of a suitable antenna, where the junction is heated by the received radiation. Sb_2Te_3 and Bi_2Te_3 thin films have ideal thermoelectric properties for this application, and deposition over patterned photoresist on suitable substrate followed by lift-off is the simplest patterning approach. Our optimization study of unpatterned sputtered films on heated substrates required temperatures exceeding 175 °C to obtain ideal thermoelectric performance. Such temperatures tend to carbonize photoresists, complicating the subsequent lift-off. Here we report the results of a new optimization study using lower substrate temperatures during sputtering followed by annealing. Our approach considers three factors in a two-level full factorial optimization experiment. The three factors are substrate temperature during sputtering, subsequent vacuum annealing temperature, and annealing time. High and low values are selected for each factor giving 8 possible combinations. A mid-point tests for curvature in the main effects. The nine depositions per material were performed on glass substrates in randomized order. Graphs of the response (Seebeck coefficient) averaged over two of the factors plotted vs the third reveal the main effects of varying each factor. Graphs of the response averaged over one of the factors and plotted vs a second factor for each value of the third factor reveal interactions between factors. Examples of device fabrication following the optimized recipe, characterization, and simulation will be presented.

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