Novel Materials
Room Ballroom A - Session NM-TuA2
Novel Oxides and Superconductors

Moderator: Dr. Matthew J. Brahlek, Oak Ridge National Laboratory

3:30pm **NM-TuA2-9 TaO_2 - The New Kid on the 5*d* Block***, Yorick Birkhölzer, A. Park, M. Barone, D. Schlom,* Cornell University

For the realization of the next generation of fast, energy-efficient nanoelectronics, there is a great need for new materials whose electrical and optical conductivities can be sensitively tuned between high (on) and low (off) states by altering a thermodynamic control parameter, e.g., strain or temperature. Unfortunately, most materials are either metallic or insulating and their conductivities cannot be changed substantially. Materials exhibiting a metal-insulator transition (MIT) at or above room temperature are quite rare, limiting their applicability in devices. The archetypical compound displaying an MIT is VO_2 with a transition temperature of 65 °C. Shortly after the discovery of the MIT in $3d^1$ VO_2[1], a similar effect was discovered in $4d^1$ NbO_2 albeit at a much higher temperature of 807 °C[2]. Thus far, the $5d^1$ analog TaO_2 has remained elusive.

Here, we show the growth of epitaxial thin films of phase-pure, rutile-like $5d^1$ TaO_2 using suboxide MBE. This recently developed flavor of MBE makes use of the TaO_2 molecular vapor emanating from a Ta_2O_5 charge in an effusion cell heated to temperatures around 1700 °C[3]. This approach avoids the notoriously unstable electron-beam evaporation of Ta metal and need for subsequent oxidation using a background gas or plasma. The latter is particularly challenging to control in the quest for TaO_2 as the stable bulk phase of tantalum oxide is the $5d^0$ compound Ta_2O_5, a band insulator without an MIT, similar to the case of $3d^0$ V_2O_5 and $4d^0$ Nb_2O_5. In the suboxide MBE approach, the Ta^{4+} is delivered to the substrate from a pre-oxidized molecular beam of TaO_2.

Unlike VO_2 that can be formed at back-end-of-line-compatible temperatures below 400 °C[4], we find that exceptionally high substrate temperatures above 1000 °C are needed to crystallize TaO_2 by suboxide MBE. Such high temperatures exceed the range of typical MBE systems but are attainable at the PARADIM Thin Film Facility, an NSF-supported national user facility[5], thanks to a recently installed CO_2 laser-based substrate heater.

Ongoing efforts entail the detailed investigation of the effect of epitaxial strain on the structural and spectroscopic properties of TaO_2 thin films on various substrates. To this end, we are employing an ensemble of X-ray, optical, and electrical transport techniques, searching for signs of a structural and electronic phase transition in this candidate $5d^1$ MIT compound.

[1] Morin, F.J., *Phys. Rev. Lett.***3**, 34 (1959)
[2] Janninck, R.; Whitmore, D., *J. Phys. Chem. Solids***27** (1966)
[3] Schwaigert, T. *et al*, *J. Vac. Sci. Technol. A***41**, 022703 (2023)
[4] Paik, H. et al., *Appl. Phys. Lett.***107**, 163101 (2015)
[5] www.PARADIM.org

3:45pm **NM-TuA2-10 Growth of $KTaO_3$, $KNbO_3$ and $KNb_xTa_{1-x}O_3$ solid solutions by Suboxide Molecular-Beam Epitaxy***, Tobias Schwaigert,* Cornell University*; S. Hazra,* Penn State University*; S. Salmani-Razaie,* Cornell University*; T. Kuznetsova,* Penn State University*; S. Ganschow,* Leibniz-Institut für Kristallzüchtung, Germany*; H. Paik,* Oklahoma State University*; D. Muller,* Cornell University*; R. Engel-Herbet,* Paul Drude Institute, Germany*; V. Gopalan,* Penn State University*; D. Schlom,* Cornell University*; K. Ahadi,* North Carolina State University

Strain-engineering is a powerful means to tune the polar, structural, and electronic instabilities of ferroelectrics. $KTaO_3$ is an incipient ferroelectric, with a very large spin-orbit coupling, in which highly anisotropic superconductivity emerges near a polar instability in electron doped samples[1, 2]. Growth of high-quality epitaxial films provides an opportunity to use epitaxial strain to finely tune electronic and polar instabilities in $KTaO_3$. $KNbO_3$ is a well-known ferroelectric with multiple structural transitions[3]. Using a molecular beam of the suboxides TaO_2 and NbO_2 emanating from effusion cells containing Ta_2O_5 or Nb_2O_5 in combination with a molecular beam of potassium emanating from an indium-potassium intermetallic in an oxidant (~10% O_3 + 90% O_2) background pressure of 1×10^{-6} Torr, $KTaO_3$, $KNbO_3$ and $KNb_xTa_{1-x}O_3$ films are grown under conditions of excess potassium in an absorption-controlled regime. Biaxial strains ranging from -0.1 % to -2.1 % are imposed on the commensurately strained $KTaO_3$ films by growing them upon $SmScO_3$, $GdScO_3$, $TbScO_3$, $DyScO_3$ and $SrTiO_3$ substrates, all with the perovskite structure. Reciprocal space mapping shows the epitaxial thin films are coherently strained to the underlying perovskite substrates provided the films are sufficiently thin. Cross-sectional scanning transmission electron microscopy does not show any extended defects and confirms that the films have an atomically abrupt interface with the substrate. X-ray diffraction rocking curves (full width at half maximum < 30 arc sec on all of the above substrates) are the narrowest reported to date for $KTaO_3$, $KNbO_3$ and $KNb_xTa_{1-x}O_3$

films grown by any technique. Laue fringes confirm that the films are smooth with a well-defined thickness. Atomic force microscopy reveals atomic steps at the surface of the grown films. SIMS measurements confirm that the films are free of indium contamination.

References

[1] Ueno K et al. Discovery of superconductivity in $KTaO_3$ by electrostatic carrier doping. Nat. Nanotechnol. 2011; 6:408

[2] Bruno FY et al. Band structure and Spin-orbital Texture of the (111)-$KTaO_3$ 2D Electron Gas. Adv. Electron. Mater. 2019; 5:1800860

[3] Hewat, A. W. Cubic-tetragonal-orthorhombic-rhombohedral ferroelectric transitions in perovskite potassium niobate: neutron powder profile refinement of the structures. J. Phys. C: Solid State Phys. 1973; 6.16:2559.

4:00pm **NM-TuA2-11 Studying Electronic Structures of Pure $SrCoO_X$ Thin Films, Ordered Phases, and Heterostructures***, Jibril Ahammad, G. Rimal,* Auburn University*; J. Sadowski,* Brookhaven National Laboratory*; G. Sterbinsky,* Argonne National Laboratory*; M. Boebinger,* Oak Ridge National Laboratory*; R. Comes,* Auburn University

$SrCoO_x$ (SCO) exhibits contrasting crystalline, electronic, and magnetic states with varying oxygen content. While in brownmillerite (BM) phase, $SrCoO_{2.5}$ is anantiferromagnetic insulator with ordered oxygen vacanices, $SrCoO_3$ is a ferromagnetic metal with the cubic perovskite (P) structure. Although SCO has been a relatively well-studied system, its growth using molecular beam epitaxy (MBE) has remained very limited. P-phase SCO films show high sensitivity to cation stoichiometry and oxygen chemical potential, with secondary phases present depending on growth conditions. In this work, we grew $SrCoO_x$ using MBE- via both shuttered and co-deposition methods- in oxygen plasma, with $2.5 \le x \le 2.87$ as suggested by X-ray diffraction (XRD). X-ray absorption study (XAS) of Co L and O K edges confirms Co^{3+} or higher cobalt oxidization states. In-situ reflection high-energy electron diffraction (RHEED) indicates excellent quality and highly epitaxial growth of our films. Stoichiometry ratios between Co and Sr were determined using in-vacuo X-ray photoelectron spectroscopy (XPS), followed by Rutherford backscattering (RBS). We grew our films on three different substrates: $LaAlO_3$ (LAO), $La_{0.3}Sr_{0.7}Al_{0.65}Ta_{0.35}O_3$ (LSAT), and $SrTiO_3$ (STO) which have lattice mismatches of - 1.0%, 1.0% and 2.0% with P-SCO respectively. Therefore, our study also provides a scope to explore strain-induced oxygen vacancies in the SCO films and their impacts on phase stability. Measurements of these phases were performed using temperature dependent transport property measurements and Scanning transmission electron microscopy (STEM). An evolution of electronic structure of 3d SCO films when coupled with 5d Ir/ Ta based systems in superlattice/double-perovskite structures can provide a further scope to study charge transfer in metastable oxide perovskites.

4:15pm **NM-TuA2-12 Synthesizing Metastable Ruddlesden-Popper Titanates by Mbe in Pursuit of Next-Generation Millimeter-Wave Tunable Dielectrics***, Matthew Barone,* Cornell University*; Z. Tian,* University of California at Berkeley*; M. Papac,* National Institute of Standards and Technology, Boulder*; B. Goodge, E. Fleck, G. Olsen,* Cornell University*; K. Lee,* Hongik University, Republic of Korea*; L. Kourkoutis,* Cornell University*; N. Orloff,* National Institute of Standards and Technology, Boulder*; L. Martin,* University of California at Berkeley*; D. Schlom,* Cornell University

While paraelectric $(Ba,Sr)TiO_3$ films were once used as tunable dielectrics in radio frequency (RF) circuits, dielectric loss above 10 GHz renders $(Ba,Sr)TiO_3$ incompatible with the high frequency future of RF electronics.[1]The related Ruddlesden-Popper titanates—$(ATiO_3)_nAO$ with A = (Ba,Sr)—have demonstrated low loss up to 100 GHz, but these experiments have used interdigitated capacitors compatible with the in-plane dielectric tunability of these phases,[2,3] rather than commercially preferable[1] metal-insulator-metal (MIM) capacitors requiring out-of-plane dielectric tunability. To achieve out-of-plane tunability in a Ruddlesden-Popper film, first-principles calculations indicate the concentration of barium and the series member, *n*, should both be maximized,[3,4] but synthesizing such films is extremely challenging. Here, we refine existing synthesis techniques to grow a high-*n* Ruddlesden-Popper (*n* = 20), containing the highest concentration of barium ever accomplished in a Ruddlesden-Popper (*A* = $Ba_{0.6}Sr_{0.4}$) as shown in Fig. 1(b).[5] With a firm grasp on the synthesis, we have demonstrated epitaxially strained heterostructures of $(ATiO_3)_nAO$ dielectric layers with metallic $SrRuO_3$ electrodes (Fig. 1(b)). Measurements confirm that such Ruddlesden-Popper films are, in fact, ferroelectric (Fig. 1(c)) and that the dielectric constant is highly tunable at room temperature (Fig. 1(d)). To assess their relevance to the future of tunable dielectrics for GHz electronics, it remains to evaluate the dielectric loss of these new phases at frequencies greater than 10 GHz.

References

[1] G. Subramanyam, M.W. Cole, N.X. Sun, T.S. Kalkur, N.M. Sbrockey, G.S. Tompa, X. Guo, C. Chen, S.P. Alpay, G.A. Rossetti, K. Dayal, L.Q. Chen, and D.G. Schlom, J. Appl. Phys. **114**, 191301 (2013).

[2] C.-H. Lee, N.D. Orloff, T. Birol, Y. Zhu, V. Goian, E. Rocas, R. Haislmaier, E. Vlahos, J.A. Mundy, L.F. Kourkoutis, Y. Nie, M.D. Biegalski, J. Zhang, M. Bernhagen, N.A. Benedek, Y. Kim, J.D. Brock, R. Uecker, X.X. Xi, V. Gopalan, D. Nuzhnyy, S. Kamba, D.A. Muller, I. Takeuchi, J.C. Booth, C.J. Fennie, and D.G. Schlom, Nature **502**, 532 (2013).

[3] N.M. Dawley, E.J. Marksz, A.M. Hagerstrom, G.H. Olsen, M.E. Holtz, V. Goian, C. Kadlec, J. Zhang, X. Lu, J.A. Drisko, R. Uecker, S. Ganschow, C.J. Long, J.C. Booth, S. Kamba, C.J. Fennie, D.A. Muller, N.D. Orloff, and D.G. Schlom, Nat. Mater. **19**, 176 (2020).

[4] K. Lee, W. Lee, M. Jeong, Y. Kim, E. Kim, H. Mun, J. Lee, C. Lee, K. Cho, D.G. Schlom, C.J. Fennie, N.M. Dawley, G.H. Olsen, and Z. Wang, U.S. Patent No. 11,133,179 B2 (2021).

[5] M.R. Barone, M. Jeong, N. Parker, J. Sun, D.A. Tenne, K. Lee, and D.G. Schlom, APL Mater. **10**, 91106 (2022).

4:30pm **NM-TuA2-13 MBE Synthesis and UV Raman Characterization of hexagonal $ScFeO_3$ films***, **Nicholas Parker**, D. Schlom,* Cornell University*; D. Tenne,* Boise State University*; M. Barone,* Cornell University

Hexagonal $ScFeO_3$ films synthesized by molecular beam epitaxy on (0001) oriented Al_2O_3 were studied by variable temperature ultraviolet Raman spectroscopy. Films were grown in a monolayer controlled method by shuttering of the MBE fluxes as well as by a co-deposition method so that properties of the resulting films could be compared. In addition, thin films were characterized by X-ray diffraction as well as atomic force microscopy. $ScFeO_3$ in the hexagonal phase is theorized to be multiferroic at near room temperature while being isostructural to $YMnO_3$ and other rare-earth ferrites. This multiferroicity is a combination of ferroelectricity and antiferromagnetic behavior often seen in the family of rare-earth ferrites, but at significantly higher temperatures in hexagonal $ScFeO_3$. The Raman spectra of hexagonal $ScFeO_3$ at room temperature are indicative of the polar hexagonal *$P6_3cm$* structure. Furthermore, the x-ray diffraction spectra of the films are correlated with hexagonal $ScFeO_3$. Atomic force microscopy provided detailed images of the surface layers of the films allowing for roughness estimates in the range of 1.5-10 nm depending on thickness and growth procedure. The temperature evolution over the range of 10-1450 K of the Raman spectra for hexagonal $ScFeO_3$ to a non-polar phase, and fitting the Raman intensities as a function of temperature provides a transition temperature of 950 K ± 50 K.

4:45pm **NM-TuA2-14 Growth and Characterization of Complex Nickelates with High Sr Concentration***, B. Paudel, L. Wang, Z. Yang, M. Bowden,* Pacific Northwest National Laboratory*; J. Liu,* Shanghai Institute of Microsystem and Information technology, China*; K. Koirala, T. Kaspar, P. Sushko, S. Chambers, **Yingge Du**,* Pacific Northwest National Laboratory

Complex nickelates $(R/A)NiO_3$ (where *R* denotes lanthanide and *A* denotes alkaline earth metals) are of great interests owing to their diverse structures and functionalities. Dynamic tunability of Ni valence states in nickelate thin films (from 1+ to 4+) has offered emergent properties such as superconductivity, enhanced electrocatalytic activity, quantum confinement effect, and metal insulator transitions. Despite many efforts, stabilization of the quadrivalent (Ni^{4+})state through Sr doping in rare earth nickelates has been proven difficult. In this talk, I will present our effort in growing perovskite $La_{1-x}Sr_xNiO_3$ in thin film and superlattice forms by oxygen-plasma assisted molecular beam epitaxy. We show that it is difficult to achieve high-quality single-phase epitaxy at higher Sr concentration (x>0.5) as bulk $SrNiO_3$ has a hexagonal phase. Phase segregation ($SrNiO_x$ to $SrNi_2O_3$ + Sr_2NiO_3) and phase transition (perovskite to hexagonal) are revealed for the end member at different growth and strain conditions by XPS, XRD, and STEM.

5:00pm **NM-TuA2-15 Sharpening the Superconducting Transition of $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$ Films with *n*=1–3 Grown by MBE***, **Y. Eren Suyolcu**, Y. Li, D. Schlom,* Cornell University

In bulk, the $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$ (i.e., Bi-cuprate) family provides the highest superconducting transition temperature—up to 105 K [1]—without highly toxic constituents like thallium or mercury. When prepared as epitaxial films, however, the superconducting transitions of this family are broad and depressed for as-grown epitaxial films, with the highest zero-resistance T_c reported to date of 97 K [2]. In this work, we use ozone-assisted MBE to grow $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$ (*n*=1–3) single-layers and bi-layers on (100) $SrTiO_3$ substrates, where weuse a non-superconducting $Bi_2Sr_2CuO_6$ (Bi-2201, *n*=1) buffer layer to reduce disorder caused by the underlying substrate. We demonstrate that combining adsorption-controlled *co-shuttered* growth and the initial precise flux calibration provides the best structural and superconducting properties for Bi-cuprate films formed at growth rates of 0.1 μm/hr or higher.

In-situ reflection high-energy electron diffraction exhibits incommensurate structural modulation and also proves the absence of any secondary phases. The structural quality of the samples is confirmed using a combination of four-circle x-ray diffraction, atomic force microscopy, and transmission electron microscopy. The superconducting properties are studied by resistivity vs temperature measurements. Bi-2201/Bi-2212 bilayers exhibit the smoothest reported surfaces with subnanometer root-mean-square (rms) roughness of ~0.4 nm and the sharpest superconducting transition width (ΔT_c) ~10 K, similar to Bi-2212 single crystals. While the $T_{c(R=0)}$ for the as-grown bilayer is low, i.e., ~50 K, this is a matter of oxygen content and can be modified via a post-growth process. This presentation focuses on achieving the high-structural and surficial quality and the sharp ΔT_c of the as-grown samples. We conclude that combining the *co-shuttered* growth and the initial precise flux calibration provides the best structural and superconducting properties [3].

References

[1] H. Maeda et al., Jpn. J. Appl. Phys. **27** (1988), L209.

[2] K. Endo et al., Nature. **355** (1992), 327.

[3] Y. E. Suyolcu et al., in preparation.

5:15pm **NM-TuA2-16 High-Temperature Superconductor FeSe Films Enabled Through Temperature and Flux Ratio Control***, **Maria Hilse**, H. Yi, C. Chang, N. Samarth,* The Pennsylvania State University*; R. Engel-Herbert,* Paul-Drude-Institut für Festkörperelektronik, Germany

FeSe, a bulk superconductor with a T_C of 9K has attracted a high level of attention since a skyrocketing boost in T_C was reported for a single unit cell (UC) layer of FeSe grown on $SrTiO_3(001)$ by molecular beam epitaxy (MBE) to as high as 100K. FeSe-$SrTiO_3$ heterostructures have since been fabricated by many groups but the record T_C proved difficult to reproduce and thus the mechanism behind it remains concealed. After extensive work in the past, the field appears to agree on certain key “ingredients” in the sample preparation that are believed essential for the boost in T_C. Those are; 1. an ultra-clean substrate surface of a double TiO_2 termination realized by a chemical and thermal *ex-situ* and/or thermal *in-situ* substrate preparation; 2. ultra-thin – one UC thickness – limit of FeSe; 3. a high number of Se vacancies in the FeSe film ensured through post-growth annealing steps in ultra-high vacuum (UHV) for several hours; 4. followed by a capping layer growth protecting FeSe against oxidation during *ex-situ* characterization. We present our findings on FeSe thin film growth by MBE and present a roadmap for high-T_C - 222% higher than the reported bulk value in *ex-situ* transport measurements - circumventing above mentioned steps 1, 2, and 3 by simple *in-situ* Se/Fe flux ratio and temperature control during FeSe growth. FeSe films of 20-UC-thickness grown at varying temperatures and Se/Fe flux ratios and the structural and morphological properties of the obtained uncapped FeSe films were analyzed. The morphology of the films showed a sensitive dependence on the growth temperature and flux ratio spanning from perfectly smooth and continuous films with atomic terraces at 450 °C growth temperature and a low flux ratio of 2.5 to exclusively disconnected island growth of large height but smooth top surfaces at lower temperatures and/or higher flux ratios. Surprisingly, the tetragonal P4/nmm crystal structure of FeSe was maintained for all investigated films and the *in-situ* observed diffraction pattern in reflection high energy diffraction also maintained the streaky pattern characteristic for smooth FeSe films even for the samples with the most pronounced island growth resulting in a root mean square atomic force microscopy roughness of more than 18nm. Smaller flux ratios than 2.5 resulted in mixed - FeSe/elemental Fe - phase samples. FeSe films grown under optimized conditions at 450°C and a flux ratio of 2.5 (but without any post-growth UHV anneal) and capped with the commonly used FeTe (300°C) and elemental Te (room temperature) layers yielded superconducting onset temperatures of about 30K and a T_C of 20K.

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