Novel Materials
Room Ballroom A - Session NM-MoA2
Strong Spin-Orbit Oxides

Moderator: Prof. Ryan Comes, Auburn University

3:30pm **NM-MoA2-9 Atomic Scale Modeling of the Hybrid Molecular Beam Epitaxy Growth Process Using Reactive Force Field Simulations***, B. Yalcin, D. Yilmaz, A. van Duin,* Pennsylvania State University*;* ***Roman Engel-Herbert*****,** Pennsylvania State University, USA, Paul-Drude-Institute for Solid State Electronics, Berlin, Germany

The hybrid molecular beam epitaxy approach for the growth of oxides – i.e. the co-supply of atomic and molecular species in their elemental and metalorganic form – has allowed accessing a self-regulated growth window for complex oxides thin films with a range of chemistries, including titanates, vanadates, stannates, and ruthenates. While it is widely accepted that the favorable growth kinetics is enabled by the volatility of the metalorganic molecules supplied, their thermal decomposition and surface reaction kinetics is complex and far from understood. For example, while it is generally assumed that the thermal decomposition of the widely employed metalorganic molecule titanium(IV)-isopropoxide (TTIP) used for the growth of titanates by hybrid MBE takes place by dissociating C-O bonds via the *β*-hydride elimination process, alternative reaction pathways, in particular in proximity of solid surface with different chemistries, such as SrO and TiO_2 terminated growth fronts, might be relevant as well.

In this talk, we present reactive force field molecular dynamics (ReaxFF-MD) and metadynamics simulations to shed light on the reaction kinetics of TTIP at the atomic scale. While the initial organic ligand pyrolysis step was spontaneous and occurred exclusively by breaking a C-O bond, albeit not always via *β*-hydride elimination in subsequent thermal decomposition stages, C-O bond dissociation events typically occurred with incomplete hydronation of the remaining Ti-containting fragment. In addition, Ti-O bond dissociation events were observed for Ti-containing molecule fragments at subsequent stages of the thermal decomposition process, challenging the simplistic picture of *β*-hydride elimination. The complete reaction scheme for the thermal decomposition of TTIP will be presented along with the reaction barriers and thermodynamic driving force for the different bond dissociation events and the role of the formal titanium oxidation state on the decomposition kinetics will be discussed, which offer a simple explanation to understand the different decomposition behavior of TTIP when interacting with the different terminations of $SrTiO_3$ surfaces. The computational approach provides a predictive and computationally inexpensive framework to identify chemical reaction pathways relevant to MBE film growth processes at the atomic scale under realistic, while experimentally relevant conditions. It can be easily expanded to different metalorganic precursor molecules, therefore allowing to develop a computationally informed engineering strategy to design MO molecules for hybrid MBE beyond the currently established chemistries.

3:45pm **NM-MoA2-10 Engineering Metal Oxidation Towards Epitaxial Growth of Complex Iridates using Molecular Beam Epitaxy***,* ***Sreejith Nair****, Z. Yang, D. Lee, S. Guo,* University of Minnesota, USA*; J. Sadowski,* Brookhaven National Laboratory*; S. Johnson,* Auburn University*; A. Saboor,* University of Delaware*; Y. Li, H. Zhou,* Argonne National Laboratory*; R. Comes, W. Jin,* Auburn University*; K. Mkhoyan,* University of Minnesota, USA*; A. Janotti,* University of Delaware*; B. Jalan,* University of Minnesota, USA

The platinum group metals like Ir and Ru have captured significant interest in the condensed matter physics and materials science community due to the exotic electronic and magnetic properties that they exhibit when combined with oxygen. The oxides of these metals provide a unique platform to study and leverage the delicate interplay between electron correlations, crystal field and spin-orbit coupling energies. High quality thin films of complex platinum group metal oxides are hence, critical to realizing new phenomena such as the predicted unconventional superconductivity in Sr_2IrO_4. However, the platinum group metals have extremely low vapor pressures and low oxidation potentials. These factors make it challenging to synthesize their oxide thin films using an ultra-high vacuum (UHV) technique like Molecular Beam Epitaxy (MBE). Here, we have addressed these challenges using a novel solid-source metal-organic MBE approach [1,2]. We demonstrate atomically precise synthesis of binary IrO_2 using $Ir(acac)_3$ as the metal-organic Ir source at substrate temperatures as low as 250 °C. The use of the metal-organic precursor allows Ir supply at source temperatures less than 200 °C and enables easy oxidation due to the +3 Ir oxidation state in the precursor. Further, by combining epitaxially strained IrO_2 thin film growth on different substrates, x-ray diffraction, electron microscopy, spectroscopy techniques, and DFT calculations, we demonstrate a vital role of epitaxial strain in Ir oxidation. Thus, epitaxial strain can be an additional tuning knob to engineer metal oxidation which can aid the conventional thermodynamic and kinetic driving forces [3].

However, the true test of metal oxidation in UHV occurs at high growth temperatures where oxidation becomes increasingly thermodynamically unfavorable. Hence, in order to examine the efficacy of the solid-source metal-organic MBE approach and to realize the elusive unconventional superconducting state, we study the synthesis of Sr_2IrO_4 thin films, which is favored at growth temperatures greater than 600-700 °C. We will present a detailed growth study, structural characterization, electrical and magneto-transport in epitaxial Sr_2IrO_4 films, along with alternative ways to tackle the Ir oxidation challenge in UHV synthesis.

References:

[1] W. Nunn et al., "Solid source metal-organic molecular beam epitaxy of epitaxial RuO_2", *APL Mater. 9, 091112 (2021)*

[2] W. Nunn et al., "Novel synthesis approach for “stubborn” metals and metal oxides", *Proc. Natl. Acad. Sciences 118, e2105713118 (2021)*

[3] S. Nair et al., "Engineering Metal Oxidation using Epitaxial Strain"*Nat. Nanotechnol. (accepted) (2023).*

4:00pm **NM-MoA2-11 Solid Source Metal-Organic Molecular Beam Epitaxy for Epitaxial $SrRuO_3$ Films***,* ***Anusha Kamath Manjeshwar****, S. Nair, A. Rajapitamahuni, R. James, B. Jalan,* University of Minnesota

The investigation of the electrical and magnetic properties of $SrRuO_3$ and its associated $Sr_{n+1}Ru_nO_{3n+1}$ Ruddlesden-Popper phases requires a high degree of control over the isolation of the desired phase and its defect density. The growth of ruthenates is fundamentally challenging because ruthenium (Ru) resists scalable evaporation and oxidation. This bottleneck complicates the growth of $SrRuO_3$ films with low defect densities using inherently low-energy, ultra-high vacuum deposition techniques such as molecular beam epitaxy (MBE). Special modifications to conventional MBE such as electron-beam assisted evaporation and ozone-assisted oxidation of Ru have, so far, enabled the best defect control or the highest residual resistivity ratios (RRR = ρ_{300K}/ρ_{2K}) in $SrRuO_3$ films among all physical vapor deposition techniques. However, these modifications are expensive and require additional interlocks to ensure safe operating conditions.

We outline a novel technique called solid source metal-organic MBE to supply a solid metal-organic precursor with pre-oxidized ruthenium with an effusion cell at $T < 200$ °C, a drastic decrease from the ~ 2000 °C required to produce comparable fluxes with elemental Ru. With this technique, we demonstrate the growth of phase pure, epitaxial, and stoichiometric $SrRuO_3$ films with robust ferromagnetism below 150 K on $SrTiO_3$ (001) substrates. We simplify the route to an adsorption-controlled growth window in $SrRuO_3$ films, growth conditions where the films can self-regulate their stoichiometry, which is a key ingredient for successful defect control in electron-beam and ozone-assisted MBE-grown $SrRuO_3$ films. We discuss the intricate relationship between cation stoichiometry, magnetic domains, and RRR in epitaxial $SrRuO_3$ films and outline new pathways for achieving low defect densities in $SrRuO_3$. Using these guidelines to optimize stoichiometry and film thickness within a growth window, we achieve a RRR = 87 for a 50 nm-thick $SrRuO_3$ film, the highest for any $SrRuO_3$ film on $SrTiO_3$ (001) substrates. We will also illustrate how solid source metal-organic MBE is a simple and cost-effective method to enhance the capabilities of conventional MBE for the defect-controlled growth of ruthenates.

4:15pm **NM-MoA2-12 Growth of Ruddlesden-Popper Ruthenates via Thermal Laser Epitaxy***,* ***Brendan D. Faeth****, F. Hensling, V. Harbola, L. Majer,* Max Planck Institute for Solid State Research, Germany*; H. Boschker,* Epiray GMBH, Germany*; W. Braun, J. Mannhart,* Max Planck Institute for Solid State Research, Germany

Thermal laser epitaxy (TLE) is a novel technique for thin film deposition which employs continuous wave lasers to simultaneously heat both the substrate and elemental sources.This laser heating approach allows for evaporation or sublimation of nearly all elements from the periodic table, ultrahigh substrate temperatures exceeding 2000 C, and broad compatibility with process gases at a wide range of pressures from UHV up to 1 Torr, among other benefits.As a result, TLE dramatically expands the parameter space available for thin film synthesis compared to existing epitaxy techniques.However, to date it has been experimentally challenging to achieve simultaneous control of multiple laser based elemental sources with the flux stability and systematic fidelity necessary for the growth of ternary or multernary systems of interest such as complex oxides.

In order to establish the capabilities of TLE for the growth of such complex oxides, we demonstrate here the successful epitaxial synthesis of several Ruddlesden-Popper phases of the Sr-Ru-O ternary oxide system via TLE. Near instant thermalization of both source elements and substrates from laser heating allows the process of thermodynamic phase control to be achieved rapidly during film deposition without the need for physical shuttering of sources.Additionally, we find that the “n=1” phase Sr_2RuO_4 can be reliably synthesized at substrate temperatures in excess of 1200 C and in a background environment of pure molecular oxygen, within an adsorption-controlled growth window that is inaccessible to conventional MBE systems.We show that films grown under these conditions demonstrate high structural, electronic, and chemical quality comparable to that of MBE-grown films.A detailed accounting of the experimental approach, growth thermodynamics, and film characterization will be discussed.

This work not only demonstrates the feasibility of TLE for the synthesis of high-quality complex oxide thin films, but also suggests new routes to achieving thin film growth in other materials systems that remain as-yet inaccessible to conventional epitaxy techniques.

4:30pm **NM-MoA2-13 Growing Clean Crystals from “Dirty” Precursors in MBE***, **Rashmi Choudhary,*** University of Minnesota, USA*; Z. Liu, J. Cai, X. Xu, J. Chu,* University of Washington*; B. Jalan,* University of Minnesota, USA

Ultra-high purity elemental sources have long been considered a prerequisite for obtaining low impurity concentration in compound semiconductors in the world of molecular beam epitaxy (MBE). Furthermore, to realize intrinsic properties, the material needs to be nearly free of intrinsic and extrinsic defects. For this reason, the use of ultra-high-purity elemental sources has been the historical practice in MBE, perhaps, for the fear that impurity elements might get incorporated into the film, making it “dirty”.

In this work, we challenge this conventional MBE wisdom by presenting an extension of the hybrid-MBE approach, known as solid-source metal-organic MBE, for growing superconducting Sr_2RuO_4 films using a solid organometallic precursor, ruthenium acetylacetonate, as a source of Ru. We grew 100 nm thick (001) Sr_2RuO_4 films on (001) LSAT substrate at 900°C substrate temperature using co-deposition of Sr, ruthenium acetylacetonate, and oxygen plasma. These films are phase-pure, single-crystalline, fully coherent, and superconducting. The superconducting transition temperature of the film is 0.85 K. In contrast to the conventional MBE, which employs ultra-pure Ru metal evaporated at ~ 2000°C as a Ru source, along with reactive ozone to obtain $Ru \rightarrow Ru^{4+}$ oxidation, the use of ruthenium acetylacetonate precursor requires significantly lower temperature for Ru sublimation (less than 200°C) and eliminates the need for ozone.

This is the first-time realization of superconducting Sr_2RuO_4 films using ozone-free MBE. By combining our results with the recent developments in hybrid-MBE, we argue that leveraging precursor chemistry will be necessary to realize next-generation breakthroughs in the synthesis of atomically precise quantum materials. Our results establish hybrid-MBE as a viable method for growing highest quality crystals and put this technique at the forefront of vacuum deposition technologies despite the use of a “dirty” chemical precursor.

4:45pm **NM-MoA2-14 MBE Growth of $BaCo_2Ru_4O_{11}$: A Metallic Ferromagnetic Hexaferrite***, **Yilin Evan Li,*** Department of Materials Science and Engineering, Cornell University*; M. Brützam,* Leibniz-Institut für Kristallzüchtung, Germany*; R. Cava,* Department of Chemistry, Princeton University*; C. Guguschev,* Leibniz-Institut für Kristallzüchtung, Germany*; D. Schlom,* Department of Materials Science and Engineering, Cornell University

Multiferroics with coupled magnetic and electric orders, although rare, hold potential for low-energy-consumption materials for logic and memory capable of electric-field control of magnetism. Barium hexaferrite ($BaFe_{12}O_{19}$) is the leading seller in today’s multi-billion-dollar magnetic ferrite market and is predicted to gain electric polarization order at room temperature in addition to its robust ferrimagnetism under in-plane, biaxial, compressive strain [1]. Epitaxial strain engineering has achieved significant success in modifying materials’ electric and magnetic ground states. For instance, the tensile strain exerted by a $DyScO_3$ substrate transforms $EuTiO_3$, an antiferromagnetic paraelectric material, into a ferroelectric ferromagnet [2]. The recent realization of single-crystal substrates of $Sr_{1.03}Ga_{10.81}Mg_{0.58}Zr_{0.58}O_{19}$(SGMZ) [3], an insulator that is isostructural to $BaFe_{12}O_{19}$, enables straining $BaFe_{12}O_{19}$ as SGMZ has a ~1.1% smaller in-plane lattice constant. In addition to strain, to induce the ferroelectric state, an epitaxial bottom electrode is needed to control the electric state for this hexaferrite multiferroic candidate. $BaCo_2Ru_4O_{11}$ is a metallic ferromagnetic oxide [4], belongs to the same hexaferrite family as $BaFe_{12}O_{19}$, and has small (~0.3%) in-plane lattice mismatch to the SGMZ substrate. Consequently, a coherent $BaCo_2Ru_4O_{11}$ epitaxial thin film on the SGMZ substrate would be ideal for straining $BaFe_{12}O_{19}$and serving as the bottom electrode of a metal-insulator-metal structure to test for ferroelectricity in this predicted strain-induced multiferroic.

Epitaxial $BaCo_2Ru_4O_{11}$thin films have not previously been reported, perhaps due to the lack of hexagonal ferrite substrates and the synthesis challenges associated with the growth of complex ruthenate epitaxial thin films. Films of $BaCo_2Ru_4O_{11}$ were grown by MBE on (0001) SGMZ substrates in an adsorption-controlled regime, similar to the way that films of $SrRuO_3$ and $CaRuO_3$ films with high resistivity ratios have been grown by MBE [5]. With matching substrates and adsorption-controlled growth, we have grown epitaxial $BaCo_2Ru_4O_{11}$thin films with resistivity ratios comparable to $BaCo_2Ru_4O_{11}$ single crystals [4].

[1] Wang, P. S., Xiang, H.J. *Physical Review X***4**, 011035 (2014).

[2] Lee, J. H. et al. *Nature***476**, 114 (2011).

[3] Guguschev, C. et al. *Crystal Growth & Design* **22 (4)**, 2557-2568 (2022).

[4] Foo, M. L. et al. *Journal of Solid State Chemistry***179**, 563-572 (2006).

[5] Nair, H. P. et al. *APL Materials***6**, 046101 (2018).

5:00pm **NM-MoA2-15 Hybrid Molecular Beam Epitaxy of $SrIrO_3$ Films and Heterostructures***, **Gaurab Rimal,** T. Tasnim, J. Ahammad,* Auburn University*; G. Sterbinsky,* Argonne National Lab*; J. Sadowski,* Brookhaven National Laboratory*; M. Boebinger,* Oak Ridge National Laboratory*; R. Comes,* Auburn University

The iridiates form a fascinating class of oxides. The high spin-orbit coupling of Ir has been predicted to lead to novel physics such as topological phases and superconductivity in ternary iridate films and heterostructures. For investigating these effects, high quality materials, including epitaxial films, are needed. The low vapor pressure of Ir, however, precludes the use of effusion cells for MBE growth using elemental iridium. Recent progress in solid-source hybrid MBE, in which metalorganic precursors are used as a cation source, has evolved for high-quality MBE growth of films containing similar low vapor-pressure elements. In this study, we use MBE with a metalorganic iridium acetylacetonate source to grow the high-quality films of $SrIrO_3$ and heterostructures of $SrIrO_3$ with $SrCoO_3$. Specifically, we discuss the role of different substrates on film properties via temperature-dependent transport, X-ray absorption and scanning transmission electron microscopy. We examine interfacial phenomena in $SrIrO_3/SrCoO_3$ heterostructures for charge transfer and novel topological magnetic behavior.

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