

Complex Oxides: Fundamental Properties and Applications Focus Topic

Room A220-221 - Session OX+EM+MI+SS-WeM

Electronic and Magnetic Properties of Complex Oxide Surfaces and Interfaces

Moderators: Yingge Du, Pacific Northwest National Laboratory, Vincent Smentkowski, GE-Research

8:00am **OX+EM+MI+SS-WeM1 Charge Transfer in Lanthanum Ferrite-Strontium Nickelate Superlattices, Le Wang, Z. Yang, M.E. Bowden**, Pacific Northwest National Laboratory; *J.W. Freeland*, Argonne National Laboratory; *Y. Du, S.A. Chambers*, Pacific Northwest National Laboratory
Charge transfer at oxide interfaces can drive emergent phenomena that do not occur in the bulk, thereby significantly enriching our fundamental understanding of these material systems and their applications. Designing oxide heterostructures and seeking new and novel interfacial phenomena has been an active area of research for some time. We have synthesized a series of $[(\text{LaFeO}_3)_m/(\text{SrNiO}_{3-d})_n]_z$ ($[(\text{LFO})_m/(\text{SNO})_n]_z$) superlattices (SLs) ($z = 7$ to 21) by oxide molecular beam epitaxy on $(\text{LaAlO}_3)_{0.3}(\text{Sr}_2\text{AlTaO}_6)_{0.7}$ (LSAT) (001) substrates. *In situ* RHEED patterns and x-ray diffraction measurements reveal a high degree of structural quality in the SLs. X-ray photoemission spectroscopy (XPS) shows that the Fe is Fe^{4+} in the $(\text{LFO}_z/\text{SNO}_1)_{21}$ SL. However, the Fe 2p binding energy shifts to lower values with increasing LFO layer thickness in $(\text{LFO}_m/\text{SNO}_1)_z$ SLs, suggesting that the volume averaged Fe valence decreases. Fe L-edge X-ray absorption spectroscopy (XAS) measurements corroborate the XPS results, indicating that Fe is 4+ for the $(\text{LFO}_3/\text{SNO}_1)_{21}$ SL and mostly 3+ for the $(\text{LFO}_5/\text{SNO}_1)_{10}$ SL. On the other hand, Ni L-edge XAS shows that Ni valence is Ni^{3+} for the $(\text{LFO}_3/\text{SNO}_1)_{21}$ SL as is also true for insulating NdNiO_3 , suggesting that the Ni layers in this SL are insulating, which is consistent with our in-plane transport measurements. However, for the $(\text{LFO}_5/\text{SNO}_1)_{10}$ SL, the Ni valence is larger than 3+. The measured energy shifts suggest that Ni is close to 4+. The thicker LFO layer in the $(\text{LFO}_5/\text{SNO}_1)_{10}$ SL may result in a larger band offset and create a potential well to trap the holes in the Ni layer, inducing the formation of Ni^{4+} . Our ongoing studies are probing the impact of the SNO layer thickness on material structure as well as the evolution of the Fe and Ni valences in $(\text{LFO}_z/\text{SNO}_1)_z$ SLs. Additional planned experimental and theoretical investigations will address how charge transfer from Fe to Ni occurs at the LFO/SNO interface, and how to stabilize the unusual high 4+ valence in Fe^{4+} and Ni^{4+} by means of interfacial engineering.

8:20am **OX+EM+MI+SS-WeM2 Self-healing Growth of LaNiO_3 on Mixed-terminated $(\text{LaAlO}_3)_{0.3}(\text{Sr}_2\text{AlTaO}_6)_{0.7}$, Friederike Wrobel, H. Hong, S. Cook, T.K. Andersen, D. Hong, C. Liu, A. Bhattacharya, D.D. Fong**, Argonne National Laboratory

Epitaxial LaNiO_3 (LNO) thin films and superlattices are known to be antiferromagnetic and weakly insulating for LNO thicknesses of 2 unit cells but paramagnetic and metallic for higher LNO thicknesses [1]. The quality of the single-crystal substrate surface, and in particular the chemical composition of the surface, is known to be a key factor governing the quality of the deposited thin film. For SrTiO_3 (001) substrates, there are well-established preparation methods to ensure that the surface is TiO_2 -terminated and atomically smooth; the only features that appear with atomic force microscopy are the regular steps and terraces associated with crystal miscut. SrTiO_3 is therefore often preferred as a substrate over other materials like $(\text{LaAlO}_3)_{0.3}(\text{Sr}_2\text{AlTaO}_6)_{0.7}$ (LSAT), whose surface composition is harder to control. Interestingly, for unknown reasons, the highest quality LaNiO_3 thin films have been grown on mixed-terminated, untreated LSAT (001) substrates [2, 3]. At present, very few detailed studies have been conducted regarding the precise influence of the substrate on thin film growth behavior due to the need for an in-situ, atomic-scale characterization technique. Exploiting an in-situ, oxide molecular beam epitaxy (MBE) chamber at the Advanced Photon Source, we were able to monitor the deposition of thin films of LNO on LSAT (001) substrates with different surface compositions. Both non-resonant and resonant (Sr K-edge) X-ray scattering measurements were conducted at several points during the growth process. We observed the formation of atomically smooth, high-quality LNO films regardless of the initial substrate surface composition, suggesting that any excess, non-stoichiometric material on the initial LSAT substrate rises to the surface during deposition. With atomic layer-by-atomic layer MBE under the right conditions, we can therefore achieve self-healing growth behavior of complex oxides on top of

mixed-terminated substrates. We will discuss details of the in-situ growth measurements and the methods used to determine the atomic and chemical structures.

1. Frano, A., et al., *Orbital Control of Noncollinear Magnetic Order in Nickel Oxide Heterostructures*. Physical Review Letters, 2013. **111**(10): p. 106804.

2. Liu, C., et al., *Counter-thermal flow of holes in high-mobility LaNiO_3 thin films*. Physical Review B, 2019. **99**(4): p. 041114.

3. Wrobel, F., et al., *Comparative study of $\text{LaNiO}_3/\text{LaAlO}_3$ heterostructures grown by pulsed laser deposition and oxide molecular beam epitaxy*. Applied Physics Letters, 2017. **110**(4): p. 041606.

8:40am **OX+EM+MI+SS-WeM3 Optoelectronics with Oxides and Oxide Heterostructures, Alexander Demkov**, University of Texas at Austin
INVITED

Si photonics is a hybrid technology combining semiconductor logic with fast broadband optical communications and optical information technologies. With the increasing bandwidth requirement in computing and signal processing, the inherent limitations in metallic interconnection are seriously threatening the future of traditional IC industry. Silicon photonics can provide a low-cost approach to overcome the bottleneck of the high data rate transmission by replacing the original electronic integrated circuits with photonic integrated circuits. The development has proceeded along several avenues including mounting optical devices based on III-V semiconductors and/or LiNbO_3 (LNO) on Si chips, incorporation of active optical impurities into Si, and utilization of stimulated Raman scattering in Si. All these approaches have had limited success. Recently, another path to Si photonics through epitaxial integration of transition metal oxide films was demonstrated when an effective electro-optic (Pockels) coefficient of BaTiO_3 (BTO) films epitaxially grown on Si via an SrTiO_3 buffer was reported to be an order of magnitude larger than that in commercially-available LNO modulators. More generally, epitaxial growth of SrTiO_3 on Si(001) enables monolithic integration of many functional perovskite oxides on Si, including ferroelectric BTO, ferromagnetic LaCoO_3 , photocatalytic TiO_2 and CoO, and many others.

In this talk, I will focus on two materials systems integrated on Si (001) and well-suited for implementation in the next-generation optical technologies: $\text{SrTiO}_3/\text{LaAlO}_3$ quantum wells and Pockels-active BTO thin film heterostructures. Both materials systems are promising for use in a wide variety of optical and electro-optical devices central to integrated photonic technologies, including quantum cascade lasers, photodetectors, electro-optic modulators and switches. The resulting devices achieve refractive index tuning with power consumption many orders of magnitude less than previously reported. Taken together, these two approaches will hopefully open the door for the development of new kinds of optical and electro-optical devices for use in integrated photonics technologies.

9:20am **OX+EM+MI+SS-WeM5 Medard W. Welch Award Lecture: Defect-Mediated Coupling of Built-in Potentials at Buried Interfaces Involving Epitaxial Complex Oxides, Scott. A Chambers**¹, Pacific Northwest National Laboratory
INVITED

Semiconductor-based devices are of broad importance, not only in electronics, but also in energy technology. Internal electric fields dictate the flow of charge that occurs both laterally and vertically. The associated potential profiles can be approximated from electronic transport data, and also calculated via Poisson-Schrodinger modeling, provided the properties of the constituent materials and interface structures are sufficiently well understood. These approaches work well for heterostructures involving, for instance, III-V semiconductors. However, when complex oxides are involved, they become unreliable because of poorly understood defects that can be present. There is, therefore, a critical need for new methods to enable the determination of band-edge profiles in heterostructures involving these materials.

The $\text{SrTiO}_3/\text{Si}(001)$ interface has been a prototypical system for understanding the materials physics and electronic structure of crystalline oxides on semiconductors. Thinner films (a few unit cells, u.c.) are known to result in flat-band heterojunctions in which the valence (conduction) band offset is large (small). However, we have recently found that thicker films (~ 30 u.c.) of $\text{SrNb}_x\text{Ti}_{1-x}\text{O}_3$ ($0 \leq x \leq 0.2$) on intrinsic $\text{Si}(001)$ result in completely different electronic structures. Transport data suggest sharp upward band bending in the Si, leading to hole gas formation at the interface, and a large (~ 2 eV) built-in potential in the SrTiO_3 , along with surface depletion. We have probed these buried interfaces using hard x-ray

¹ Medard W. Welch Award Winner

Wednesday Morning, October 23, 2019

photoelectron spectroscopy (HAXPES). The resulting core-level spectra exhibit unusual features not seen in thinner films, and not credibly ascribed to secondary phases or many-body effects. In order to interpret these line shapes, we hypothesize that they result from large built-in potentials within the system. We have developed an algorithm to extract these potential profiles by fitting heterojunction spectra to linear combinations of spectra from phase-pure, flat-band materials, summed over layers within the probe depth, each with a binding energy characteristic of the potential at each depth. This approach leads to excellent agreement with experiment and band-edge profiles completely consistent with those from transport data. Moreover, we find that the built-in potentials extracted from HAXPES on the Si side of the interface are in quantitative agreement with those resulting from solving Poisson's equation using the SIMS profile for in-diffused oxygen from the STO. Oxygen is a shallow donor in Si, and assuming 100% donor ionization, along with the ^{18}O SIMS depth profile, leads to near-perfect agreement with HAXPES.

11:20am **OX+EM+MI+SS-WeM11 Structural and Dielectric Characterization of Epitaxial Entropy-Stabilized Oxide Thin Films, George Kotsonis, J.-P. Maria, Pennsylvania State University**

The emergence of entropy-stabilized oxides (ESOs) represents a new paradigm for complex oxide engineering. The large configurational entropy of ESOs facilitates mixing of chemically dissimilar cations in significant proportions. ESO research continues to intensify as the oxide community works toward a thorough understanding of structure-property-synthesis relationships. Due to inherent metastability, high energy, non-equilibrium synthesis techniques are well suited for ESO fabrication. In particular, laser ablation has excelled at producing high quality epitaxial ESO thin films, which provide a platform for fundamental characterization.

We present the growth and characterization of $\text{Ba}(\text{Ti}_{0.2}\text{Sn}_{0.2}\text{Zr}_{0.2}\text{Hf}_{0.2}\text{Nb}_{0.2})\text{O}_3$ and similar Barium-based perovskite structured ESO thin films grown by laser ablation. Crystal structure, surface morphology, and optical properties are characterized by X-ray diffraction, atomic force microscopy, and ellipsometry respectively. Epitaxial thin film capacitor structures were fabricated to characterize the frequency, voltage, and temperature dependence of electrical properties.

By exploiting the entropy-stabilized nature of ESOs, we demonstrate the incorporation of significant amounts of aliovalent cation pairs (e.g. $\text{Sc}^{3+}\text{Ta}^{5+}$) in hopes of producing nano-polar regions supporting a dispersive dielectric response similar to relaxor ferroelectrics. Additionally, we explore compositional space in search of a phase boundary between a high-symmetry ESO phase and a lower symmetry end-member. Compositions at such a boundary may exhibit phase instability and enhanced dielectric functionality similar to compositions at or near a morphotropic phase boundary. The compositional degrees of freedom available in ESO systems provide new avenues for property tuning and studying the effects of extreme chemical disorder on dielectric properties.

11:40am **OX+EM+MI+SS-WeM12 Oxygen Vacancy-Mediated Epitaxy: $\text{TiO}_2(111)/\text{Al}_2\text{O}_3(0001)$ and Ferromagnetic $\text{Cr}_2\text{O}_3(0001)/\text{TiO}_2(111)$, C. Ladewig, F. Anwar, Jeffrey Kelber, University of North Texas; S.Q.A. Shah, P.A. Dowben, University of Nebraska-Lincoln**

The formation of all-oxide heterostructures comprising multiferroic oxides interfaced with appropriate semiconducting substrates is a promising path towards low power, voltage-switchable spintronics, including non-volatile memory and multi-functional logic devices. At the same time, the necessary scaling of film thicknesses to the nm range can induce structures and properties sharply different than those of the bulk. We report here in situ XPS, LEED, EELS and ex-situ MOKE data on the growth and properties of $\text{Cr}_2\text{O}_3(0001)$ on $\text{TiO}_{1.7}(111)$ on $\text{Al}_2\text{O}_3(0001)$. The data indicate that the presence of O vacancies during film growth can mediate the further growth of oxides with unusual structures and properties. These data show that (a) O vacancies during initial stages of film growth yield a TiO_2 film of an unusual crystallographic orientation and structure; and that (b) this leads to growth of an epitaxial Cr_2O_3 layer exhibiting magnetic ordering above the expected Néel temperature of thin film chromia - indicative of a strained chromia lattice due to epitaxial growth on a substrate with a lattice constant of 5.1 Å, compared to the bulk chromia lattice constant of 4.9 Å. Molecular beam epitaxy (MBE) of Ti at 500 K in 10^{-6} Torr O_2 on $\text{Al}_2\text{O}_3(0001)$ initially yields $\text{TiO}_{1.7}(111)$ with the structure of corundum phase Ti_2O_3 ($a = b = 5.1$ Å). Further deposition and annealing in O_2 results in stoichiometric $\text{TiO}_2(111)$, but with the same lattice structure and orientation as $\text{Ti}_2\text{O}_3(111)$, and with a total thickness of 5 nm. This is sharply different from the generally observed growth of $\text{TiO}_2(001)$ on $\text{Al}_2\text{O}_3(0001)$. MBE of ~ 1 monolayer of Cr on $\text{TiO}_2(111)$ yields hexagonally-ordered Cr_2O_3

and the formation of titania oxygen vacancies. MOKE measurements confirm that this chromia layer is magnetically ordered at 280 to 315 K, likely antiferromagnetically ordered, with exchange bias coupling to the $\text{TiO}_{1.7}(111)$ substrate. O vacancies in the $\text{TiO}_2(111)$ lattice exhibit weak ferromagnetic behavior, as is evident in the In-plane MOKE, enhancing the canting of the magnetism away from the thin film normal, which is expected for the $\text{Cr}_2\text{O}_3(0001)$ alone. These data demonstrate that careful control of initial growth conditions and film stoichiometry during oxide MBE can template the subsequent growth of stoichiometric oxide heterostructures with non-bulk like structures and properties.

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12:00pm **OX+EM+MI+SS-WeM13 Incorporation of Ti into Epitaxial Films of Magnetite, Tiffany Kaspar, S.R. Spurgeon, D.K. Schreiber, S.D. Taylor, M.E. Bowden, S.A. Chambers, Pacific Northwest National Laboratory**

Magnetite, Fe_3O_4 , exhibits metallic conductivity via electron hopping between Fe^{2+} and Fe^{3+} occupying octahedral sites in the spinel lattice. As Ti^{4+} is doped into the octahedral sites of magnetite (the titanomagnetite series), an equal fraction of Fe^{3+} is reduced to Fe^{2+} to maintain charge neutrality. The site occupancies of Fe^{2+} and Fe^{3+} determine the transport properties of the titanomagnetite series; the end-member ulvöspinel, Fe_2TiO_4 , exhibits *p*-type semiconducting transport properties. The $\text{Fe}^{2+}/\text{Fe}^{3+}$ site occupancy remains controversial, but is likely in part a function of the lattice strain induced by doping smaller Ti^{4+} into the lattice. Here, we have deposited titanomagnetites and ulvöspinel as well-defined epitaxial thin films on MgO , MgAl_2O_4 , and Al_2O_3 substrates by oxygen-plasma-assisted molecular beam epitaxy. The incorporation of Ti into the magnetite lattice is found to depend strongly on deposition conditions and substrate orientation. We have characterized the crystalline structure, phase segregation, and surface morphology with XRD, STEM/EDS, APT, and AFM, and related these to the kinetic and thermodynamic factors determined by the deposition conditions. The Fe valence state is evaluated with *in situ* XPS. The impact of film structure and Fe oxidation state on the electrical transport properties of the films will be discussed.

Author Index

Bold page numbers indicate presenter

— A —

Andersen, T.K.: OX+EM+MI+SS-WeM2, **1**

Anwar, F.: OX+EM+MI+SS-WeM12, **2**

— B —

Bhattacharya, A.: OX+EM+MI+SS-WeM2, **1**

Bowden, M.E.: OX+EM+MI+SS-WeM1, **1**;
OX+EM+MI+SS-WeM13, **2**

— C —

Chambers, S.A.: OX+EM+MI+SS-WeM1, **1**;
OX+EM+MI+SS-WeM13, **2**; OX+EM+MI+SS-
WeM5, **1**

Cook, S.: OX+EM+MI+SS-WeM2, **1**

— D —

Demkov, A.A.: OX+EM+MI+SS-WeM3, **1**

Dowben, P.A.: OX+EM+MI+SS-WeM12, **2**

Du, Y.: OX+EM+MI+SS-WeM1, **1**

— F —

Fong, D.D.: OX+EM+MI+SS-WeM2, **1**

Freeland, J.W.: OX+EM+MI+SS-WeM1, **1**

— H —

Hong, D.: OX+EM+MI+SS-WeM2, **1**

Hong, H.: OX+EM+MI+SS-WeM2, **1**

— K —

Kaspar, T.C.: OX+EM+MI+SS-WeM13, **2**

Kelber, J.A.: OX+EM+MI+SS-WeM12, **2**

Kotsonis, G.N.: OX+EM+MI+SS-WeM11, **2**

— L —

Ladewig, C.: OX+EM+MI+SS-WeM12, **2**

Liu, C.: OX+EM+MI+SS-WeM2, **1**

— M —

Maria, J.-P.: OX+EM+MI+SS-WeM11, **2**

— S —

Schreiber, D.K.: OX+EM+MI+SS-WeM13, **2**

Shah, S.Q.A.: OX+EM+MI+SS-WeM12, **2**

Spurgeon, S.R.: OX+EM+MI+SS-WeM13, **2**

— T —

Taylor, S.D.: OX+EM+MI+SS-WeM13, **2**

— W —

Wang, L.: OX+EM+MI+SS-WeM1, **1**

Wrobel, F.: OX+EM+MI+SS-WeM2, **1**

— Y —

Yang, Z.: OX+EM+MI+SS-WeM1, **1**