

Thin Films Division

Room A122-123 - Session TF+EM+MI+MN+OX+PS-MoM

Functional Thin Films: Ferroelectric, Multiferroics, and Magnetic Materials

Moderators: Christophe Vallee, LTM, Univ. Grenoble Alpes, CEA-LETI, France, Jessica Kachian, Intel Corporation

8:20am **TF+EM+MI+MN+OX+PS-MoM1 A Room-Temperature Magnetolectric Multiferroic made by Thin Film Alchemy, D.G. Schlom, Megan Holtz, Cornell University INVITED**

Materials that couple strong ferroelectric and ferromagnetic order hold tremendous promise for next-generation memory devices. Meticulous engineering has produced novel ferroelectric and multiferroic materials, although known single-phase multiferroics remain limited by antiferromagnetic or weak ferromagnetic alignments, by a lack of coupling between the order parameters, or by having properties that emerge only well below room temperature. Here we construct single-phase multiferroic materials in which ferroelectricity and strong magnetic ordering are coupled near room temperature. Starting with hexagonal LuFeO_3 —a geometric ferroelectric with planar rumpling—we introduce individual monolayers of ferrimagnetic LuFe_2O_4 within the LuFeO_3 matrix, that is, $(\text{LuFeO}_3)_m/(\text{LuFe}_2\text{O}_4)_1$ superlattices. The rumpling of the LuFeO_3 drives the ferrimagnetic LuFe_2O_4 into a ferroelectric state, reducing the LuFe_2O_4 spin frustration. This increases the magnetic transition temperature to 281K for $m=9$. Moreover, the ferroelectric order couples to the ferrimagnetism, enabling direct electric-field control of magnetism at 200 kelvin. Further, charged ferroelectric domain walls align at LuFe_2O_4 layers, resulting in charge transfer which increases the magnetic moment. We are currently pursuing higher temperature multiferroics by incorporating cubic spinels with high magnetic ordering temperatures, such as CoFe_2O_4 , into the LuFeO_3 matrix. Our results demonstrate a design methodology for creating higher-temperature magnetolectric multiferroics through epitaxial engineering.

9:00am **TF+EM+MI+MN+OX+PS-MoM3 Magnetic Losses in FeGa/NiFe/Al₂O₃ Laminates for Strain-Mediated Multiferroic Micro-Antenna Applications, Kevin Fitzell, A. Acosta, C.R. Rementer, D.J. Schneider, Z. Yao, University of California, Los Angeles; C. Dong, Northeastern University; M.E. Jamer, D. Gopman, J. Borchers, B. Kirby, National Institute of Standards and Technology (NIST); N. Sun, Northeastern University; Y. Wang, G.P. Carman, J.P. Chang, University of California, Los Angeles**

The ability to reduce the size of antennae would enable a revolution in wearable and implantable electronic devices. Multiferroic antennae, composed of individual ferromagnetic and piezoelectric phases, could reduce antenna size by up to five orders of magnitude through the efficient coupling of magnetization and electric polarization via strain. This strategy requires a material with strong magnetoelastic coupling and acceptable magnetic losses at high frequency.

Galfenol ($\text{Fe}_{84}\text{Ga}_{16}$ or FeGa) is a promising candidate material due to its large magnetostriction (200 μe), large piezomagnetic coefficient (5 ppm/Oe), and high stiffness (60 GPa), but it is highly lossy in the GHz regime. On the other hand, Permalloy ($\text{Ni}_{81}\text{Fe}_{19}$ or NiFe) is a soft magnetic material that has very low loss in the GHz regime, with a ferromagnetic resonance (FMR) linewidth of 10 Oe, but almost no magnetostriction. In this work, nanoscale laminates containing alternating layers of FeGa and NiFe were fabricated via DC magnetron sputtering to combine the complementary properties of the two magnetic phases, resulting in a composite material with a small coercive field, narrow FMR linewidth, and high permeability (Rementer et al., 2017). Optical magnetostriction measurements confirmed that these laminates retain the large saturation magnetostriction of FeGa (200 μe) while enhancing the piezomagnetic coefficient (7 ppm/Oe), allowing for optimal piezomagnetic actuation at substantially reduced magnetic bias fields. Furthermore, multiferroic composites incorporating these magnetic laminates were studied via polarized neutron reflectometry, demonstrating uniform rotation of the individual layers' magnetization with an applied electric field across distances much larger than the exchange length of either material.

Due to the metallic nature of these FeGa/NiFe multilayer composites, however, resulting devices would be inefficient due to the generation of eddy currents at high frequency. To mitigate these losses, ultrathin layers of Al_2O_3 were incorporated into the multilayer materials to reduce the

conductivity and mitigate the generation of eddy currents. The effect of Al_2O_3 thickness, FeGa:NiFe volume ratio, and multilayer architecture on the soft magnetic properties was also studied, resulting in a 50% reduction in the FMR linewidth. Optimized magnetic laminates were shown to exhibit a small coercive field (<20 Oe), narrow ferromagnetic resonance linewidth (<50 Oe), and high relative permeability (>500) while maintaining excellent magnetoelastic coupling, showing great promise for the use of FeGa/NiFe/ Al_2O_3 laminates in strain-mediated micro-scale communications systems.

9:20am **TF+EM+MI+MN+OX+PS-MoM4 Multiferroic Gd-substituted HfO₂ Thin Films, John Hayden, F. Scurti, J. Schwartz, J.-P. Maria, Pennsylvania State University**

Modern ferroelectric technologies utilize perovskite structured materials, which have limited Si compatibility and modest bandgaps requiring thick films to reduce leakage current, hindering their implementation in realizable thin film devices. HfO_2 has been extensively researched as a gate dielectric thin film with excellent Si processing compatibility and has recently been found to exhibit ferroelectricity induced by a combination of impurity substitution, mechanical confinement by capping, intergranular surface area, and film thickness effects. This work investigates the microstructural characteristics, the ferroelectric response, and the potential for concomitant magnetic properties in sputtered Gd:HfO₂ thin films.

Gd-substituted HfO_2 thin films are a promising candidate as a multiferroic material, due to the presence of the magnetically active Gd^{3+} ion. Though substituting with Gd is known to induce ferroelectricity in HfO_2 , the magnetic properties of Gd:HfO₂ have yet to be studied in depth. In this study, Gd:HfO₂ films are fabricated on TaN substrates by radio frequency sputtering of a composite Gd metal and HfO_2 oxide target in a mixed Ar and O_2 atmosphere. Grazing incidence x-ray diffraction is used to evaluate the suppression of the paraelectric monoclinic phase and stabilization of the ferroelectric orthorhombic phase. Electrical polarization measurements are used to study the room temperature spontaneous polarization in TaN/Gd:HfO₂/TaN metal-insulator-metal capacitors. Surface morphology of the films is characterized using atomic force microscopy, while magnetic properties are measured by variable temperature magnetometry. Initial magnetometry shows that Gd-substituted HfO_2 exhibits remnant magnetization at room temperature.

The scalability and simplicity of Gd:HfO₂, if it exhibits magnetolectric coupling, make it an attractive model system for future developments in thin film multiferroics, having potential impacts for spintronics and other magnetolectronic devices.

9:40am **TF+EM+MI+MN+OX+PS-MoM5 Epitaxial Growth of Antiferromagnetic NiO Films by Off-axis Sputtering for Spintronic Devices, A. Churikova, G.S.D. Beach, Massachusetts Institute of Technology; Larry Scipioni, A. Shepard, J. Greer, T. Newhouse-Ilige, PVD Products, Inc.**

High-quality epitaxial growth of antiferromagnetic thin films is essential for future spintronic devices, as it allows small antiferromagnetic domain sizes and efficient electrical manipulation of domain walls via reading and writing currents. Antiferromagnetic materials are candidates for ultrafast operation due to THz antiferromagnetic spin dynamics, high packing densities due to the absence of stray magnetic fields, and stability due to insensitivity to external magnetic fields [1,2]. Meanwhile, the long spin diffusion lengths [3] and theoretically predicted superfluid transport of spin currents [4] in antiferromagnetic insulators are crucial for low-power device operation. The electrical control of magnetic spin textures has been thus far realized in epitaxially grown NiO on MgO substrates [5] and ferrimagnetic maghemite ($\gamma\text{-Fe}_2\text{O}_3$) and magnetite (Fe_3O_4) thin films [6].

We report the preparation of antiferromagnetic NiO thin films with (111) orientation on c-plane sapphire (1000) substrates by off-axis RF magnetron sputtering from a NiO target. The off-axis angle was 45°, and the sputtering pressure was 5 mTorr. Samples were grown with thicknesses ranging from 5 – 50 nm, and with growth temperatures from room temperature to 600°C, to determine optimum conditions. Structural characterization by x-ray diffraction demonstrates a high degree of epitaxy across a range of deposition temperatures and thicknesses. The deposition temperature and thickness dependence of epitaxial quality is investigated, with a characterization of the strain state, mosaicity, and crystallographic relationship between substrate and film. Evidence for antiferromagnetic order forming domains in NiO is provided via magnetic characterization of the films. Our results are essential for the optimization of the fabrication of high quality epitaxial antiferromagnetic films for practical spintronics devices.

Monday Morning, October 21, 2019

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10:00am **TF+EM+MI+MN+OX+PS-MoM6 Structural and Magnetic Properties of CoPd Alloys for Non-Volatile Memory Applications**, *S. Gupta, J.B. Abugri, B.D. Clark*, University of Alabama; *P. Kominou*, Aristotle University of Thessaloniki; *Sujan Budhathoki, A.J. Hauser, P.B. Visscher*, University of Alabama

A study of perpendicular magnetic anisotropy (PMA) CoPd alloys is presented as a simple means of pinning MgO-based perpendicular magnetic tunnel junctions (pMTJs) for spin transfer torque magnetic tunnel junction (STT-MRAM) applications. A compositional study of the $\text{Co}_x\text{Pd}_{100-x}$ alloys at 50 nm thickness showed that the maximum coercivity and anisotropy was found for $\text{Co}_{25}\text{Pd}_{75}$. Perpendicular magnetic tunnel junction stacks were deposited using different compositions of CoPd. Current-in-plane tunneling measurements indicated that the TMR values roughly correlated with the coercivity and anisotropy of the single layers. A thickness study indicated that the alloy was fully perpendicular for thicknesses as low as 20 nm. Various seed layers were employed to optimize the coercivity of the $\text{Co}_{25}\text{Pd}_{75}$ layer. Magnetometry, X-ray diffraction (XRD), scanning electron microscopy (SEM) and high resolution transmission electron microscopy studies were carried out to relate the magnetic and structural properties of these layers. These studies showed that the highest coercivity $\text{Co}_{25}\text{Pd}_{75}$ was achieved on a seed layer of Ta/Pd which helped to crystallize the CoPd layer in an fcc (111) orientation.

10:40am **TF+EM+MI+MN+OX+PS-MoM8 Size Effects of the Electromechanical Response in Ferroic Thin Films: Phase Transitions to the Rescue**, *Nazanin Bassiri-Gharb*, Georgia Institute of Technology
INVITED

Silicon-integrated ferroelectric thin films have been leveraged over the last two decades for fabrication of high performance piezoelectric microelectromechanical systems (MEMS) devices. Ceramic $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ (PZT) thin films have been often the material of choice, due to their large electromechanical response, especially at morphotropic phase boundary compositions (MPB at $x \sim 0.52$), where co-existence of multiple crystallographic distortions can enhance extrinsic electromechanical contributions. However, ferroelectric thin films suffer from extrinsic size effects that lead to deteriorated piezoelectric properties in thin and ultrathin films. Here we report on different strategies for processing of thin films with enhanced piezoelectric response with respect to traditionally processed PZT thin films.

Specifically, we will discuss preparation of superlattice-like polycrystalline PZT thin films through chemical solution depositions, polycrystalline relaxor-ferroelectric thin films (PMN-PT), and finally alternative non-ferroelectric compositions, where the electric field-induced phase transitions can result in substantial enhancement in thinner films, even where traditional

11:20am **TF+EM+MI+MN+OX+PS-MoM10 Ferroelectrics Meet Ionics in the Land of van der Waals**, *S. Neumayer*, Center for Nanophase Materials Sciences, Oak Ridge National Laboratory; *J. Brehm*, Vanderbilt University; *M.A. McGuire*, Oak Ridge National Laboratory; *M.A. Susner*, Air Force Research Laboratory; *E. Eliseev*, National Academy of Sciences of Ukraine; *S. Jesse*, *S.V. Kalinin*, Center for Nanophase Materials Sciences, Oak Ridge National Laboratory; *A.N. Morozovska*, National Academy of Sciences of Ukraine; *S. Pantelides*, Vanderbilt University; *N. Balke*, **Petro Maksymovych**, Center for Nanophase Materials Sciences, Oak Ridge National Laboratory

Van der Waals crystals of metal thiophosphates can be thought of as derivatives of transition metal dichalcogenides where 1/3 of metal atoms is replaced with diphosphorous, thereby stabilizing the remaining 2/3 of metal ions in low oxidation states.1 Consequently, thiophosphates enable ultrathin magnetic, ferroelectric and Mott insulating materials, in q2D

materials while also providing new opportunities for multifunctional interfaces .

Of particular interest is CuInP_2S_6 , where ferroelectricity emerges out of ionically conducting state .2,3 In this work, we discuss unusual and perhaps anomalous properties observed in CuInP_2S_6 in both states.

CuInP_2S_6 exhibits giant negative electrostriction ($Q_{33} = -3.2 \text{ m}^4/\text{C}^2$), which leads to large piezoelectric coefficients despite small polarization values and increase of T_c with applied pressure. It's the only material other than polymer PVDF for which such behavior is experimentally confirmed. Density functional theory reveals that the reason for negative electrostriction is a slight movement of Cu ions into the van der Waals gap due to anharmonicity of the potential well.4 Moreover, under high compressive strain, Cu starts to form interlayer bonds with sulfur across the van der Waals gap, leading to an additional phase of high polarization. Consequently, the potential distribution exhibits 4 instead of the usual two minima - a quadruple well, that is precisely tunable by strain. In the paraelectric state above $\sim 70^\circ\text{C}$, Cu ion mobility drastically increases. Intriguingly, Cu can be reversibly extracted out of the lattice without visible damage. Finally, the selenide sibling $\text{CuInP}_2\text{Se}_6$, exhibits a lower transition temperature and propensity toward antiferroelectric ordering under the effect of depolarizing fields. In this material, we have for the first time observed piezoelectric response confined to domain walls (opposite to ferroelectrics), fulfilling the long-standing predictions for polar antiferroelectric domain walls and providing a new model system for emergent properties of topological defects in ferroic order parameter fields.

Research sponsored by Division of Materials Science and Engineering, Basic Energy Sciences, US Department of Energy. Microscopy was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

1Susner et al, *Adv. Mater.* **29**,1602852 (2018)

2Neumayer et al, *Phys. Rev. Materials* **3**, 024401 (2019)

3Balke et al, *ACS Appl. Mater. Interfaces* **10**, 27188 (2018)

4Brehm et al, in review

11:40am **TF+EM+MI+MN+OX+PS-MoM11 Adsorption-controlled Epitaxial Growth of the Hyperferroelectric Candidate LiZnSb on GaSb (111)**, *D. Du, P. Strohbeen*, University of Wisconsin - Madison; *H. Paik*, Cornell University; *C. Zhang, P. Voyles, Jason Kawasaki*, University of Wisconsin - Madison

A major challenge for ferroelectric devices is the depolarizing field, which competes with and often destroys long-range polar order in the limit of ultrathin films. Recent theoretical predictions suggest a new class of materials, termed hyperferroelectrics [1], should be immune to the depolarizing field and enable ferroelectric devices down to the monolayer limit. Here we demonstrate the epitaxial growth of hexagonal LiZnSb , one of the hyperferroelectric candidate materials, on GaSb (111) substrates. Due to the high volatility of all three atomic species, we find that stoichiometric films can be grown in a thermodynamically adsorption-controlled window, using an excess zinc flux. Outstanding challenges remain in controlling the point defects of LiZnSb and in controlling polytypism. While the films primarily grow in a hexagonal "stuffed wurtzite" phase (space group $P6_3mc$), which is has the desired polar structure, there exists a competing cubic "stuffed zincblende" polymorph that is nonopolar ($F-43m$). We will discuss our strategy towards controlling defects and polytypism in LiZnSb , which is based in large part on the wurtzite - zincblende polytypism observed in InAs . We will also present preliminary electrical measurements on phase pure ferroelectric capacitor structures.

This work was supported by the Army Research office (W911NF-17-1-0254) and the National Science Foundation (DMR-1752797).

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Electronic Materials and Photonics Division Room A214 - Session EM+OX+TF-TuA

Nikolaus Dietz Memorial Session: Wide and Ultra-wide Band Gap Materials and Devices

Moderators: Seth King, University of Wisconsin - La Crosse, David Aspnes, North Carolina State University

2:20pm **EM+OX+TF-TuA1 Nitride-Based Semiconducting Materials: A Long Pathway to Advanced Nuclear Detection Capabilities, Vincent Woods, L. Hubbard**, Pacific Northwest National Laboratory; **Z. Sitar**, North Carolina State University; **A.Y. Kozhanov**, Georgia State University **INVITED**

This energetic talk will focus primarily on the development of advanced nitride-based avalanche photodiode devices but will also highlight the many contributions that Nikolaus Dietz made to the field of real-time optical characterization, materials development and advanced growth techniques. Iterative development and advances in growth techniques and characterization have allowed sufficient improvement in materials quality to show demonstrable gain in Avalanche Photodiode Detector (APD) device structures currently being produced for nuclear detection applications. This contribution will present the structural and optoelectronic properties of GaN/AlGaIn heterostructures grown by Metal Organic Chemical Vapor Deposition (MOCVD) on AlN, GaN and sapphire templates/substrates. The target parameters for the materials heterostructures have been modeled for utilization in APD structures operating in the UV region. Optical modeling has improved absorption within the heterojunction as well as maximized light trapping within the device. Electronic modeling has determined the optimal dopant concentrations for maximum impact ionization rate, as well as tolerance to defects and unintentional doping. This application required advances in the defect densities, surface morphology, and interfaces. Surface morphological and structural properties of the GaN/AlGaIn heterostructures are analyzed by Atomic Force Microscopy (AFM), and high resolution transmission electron microscopy (TEM). Recent results related to the gain of the final APD device will be presented.

3:20pm **EM+OX+TF-TuA4 Low Temperature Growth of InN by Atomic Layer Epitaxy, Charles R. Eddy, Jr.**, U.S. Naval Research Laboratory; **S.G. Rosenberg, J.M. Woodward**, American Society for Engineering Education (residing at U.S. Naval Research Laboratory); **K.F. Ludwig**, Boston University; **N. Nepal**, U.S. Naval Research Laboratory

Wurtzite indium nitride (InN) has direct bandgap of about 0.7 eV with large phonon gap and is an attractive semiconductor material for application in various areas, e.g. optical, electrical, optoelectronic, and spintronic device technologies [1]. InN and its alloys with GaN and AlN (III-N) have therefore found application in a variety of technologies such as high power transistors, emitters, detectors, and solar-cells. The relatively high growth temperature of common III-N synthesis techniques has impeded further development and application of the materials due to challenges with miscibility gaps and strain related to thermal expansion mismatch with non-native substrates. To address these challenges, plasma assisted atomic layer epitaxy (PA-ALEP) offers a new approach to low temperature III-N growth and can be used to epitaxially grow InN by using alternative pulses of trimethylindium and nitrogen plasma [2]. We report on development of the PA-ALEP process for InN growth on sapphire and gallium nitride substrates demonstrating the self-limited growth windows as a function of temperature and pulse durations in the process. We benchmark the quality of our films compare to those grown by Dietz et al. by high pressure CVD [3]. The process produces quality, crystalline semiconductor films with properties comparable to those grown by conventional methods at temperatures roughly 2X higher. Beyond that, the PA-ALEP process affords realization of InN containing ternary nitrides with aluminum and gallium that are not possible with conventional growth methods. Further, the unique, non-thermal equilibrium process enables realization of cubic (rock salt) phases on InN. In order to better understand nucleation and growth mechanisms involved in the PA-ALEP process, we employ in situ X-ray scattering methods using synchrotron radiation. We have determined that the growth proceeds largely by a Stranski-Krastinov process on either sapphire or gallium nitride. Further, we have investigated the impact of components of the PA-ALEP cycle on the growth process [4], in particular the plasma pulse time. Here we see that pulse time can affect the nature of nucleation from bimodal nucleation to single mode nucleation to degraded

growth as pulse time increases from 15 seconds to 30 seconds. These and other nucleation and growth behaviors will be highlighted.

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4:20pm **EM+OX+TF-TuA7 Stoichiometry- and Orientation-Dependent Native Point Defects of MOCVD-Grown ZnGeN₂ Films, Micah Haseman, D. Ramdin, R. Karim**, The Ohio State University; **D. Jayatunga**, Case Western Reserve University; **H. Zhao**, The Ohio State University; **K. Kash**, Case Western Reserve University; **L.J. Brillson**, The Ohio State University

Heterovalent ternary II-IV-nitrides like ZnGeN₂ are attracting increased interest due to their close relation to technologically important III-nitrides such as GaN. Unlike many III-nitrides, the constituents of ZnGeN₂ are more earth-abundant with potential for more versatile optoelectronic lattice matching. Essential to II-IV-nitride device application is the control of native point defects and subsequent manipulation of doping and carrier compensation. In many wide band gap binary semiconductors such as GaN or ZnO the most thermodynamically stable defects are cation or anion vacancies whereas stable defects in ternary alloys may include antisites, interstitials, and their complexes as well as H interstitials and complexes. Thus identification of native point defects in ZnGeN₂ and other ternaries can be challenging. Using depth-resolved cathodoluminescence spectroscopy (DRCLS), we have observed multiple deep level defects in MOCVD-grown ZnGeN₂ films. Excitation depths obtained via Monte Carlo simulations for varying incident electron beam energies provide depth-resolution for the cathodoluminescence spectra which reveal defects that extend throughout the deposited ZnGeN₂ film and are not localized near the free surface nor the film-substrate interface, therefore, unless these defects are unintentional impurities, they must be native point defects. Density functional theory (DFT) predicts the most thermodynamically stable native point defects are in fact Zn_{Ge} and Ge_{Zn} antisites and the n-type nature of the films studied suggests that Zn_{Ge} acceptor is the most favorable defect to form [1]. We used off-stoichiometric films to identify luminescence features due to gap state transitions from specific defects. For Zn-rich films (Zn/Ge = 1.15), we observe an additional defect feature at 2.4 eV corresponding to a near mid-gap state. DFT band structures for ZnGeN₂ show that Zn_{Ge} antisites create gap states just below mid-gap, consistent with the n-type Fermi level and with the Zn-rich films. In addition, we observe strong variation in these mid-gap states with Al₂O₃ vs GaN substrate growths as well as an Al₂O₃ orientation dependence. DRCLS's ability to probe electronic structure on a near-nanometer scale enables us to probe defect variations with stoichiometry as growth conditions are varied within the outer tens of nanometers - a nanoscale testbed to identify defects. Identifying and controlling such defects using growth processes can enable advances in ZnGeN₂ for next generation electronic device applications. The authors gratefully acknowledge support from NSF grants DMR-18-00130 and DMREF 1533957.

¹Skachkov et. al. Phys. Rev. B 93, 155202 (2016)

4:40pm **EM+OX+TF-TuA8 Low-temperature Growth of Wide Bandgap Nitride and Oxide Thin Films via Plasma-assisted Atomic Layer Deposition: Influence of rf-plasma Source and Plasma Power, Necmi Biyikli, S. Ilhom, A. Mohammad, D. Shukla**, University of Connecticut

Plasma-assisted atomic layer deposition (PA-ALD) provides an alternative way to grow wide bandgap materials at substantially reduced substrate temperatures (lower than 400°C) when compared to conventional epitaxial growth techniques. While majority of the published literature indicate polycrystalline or amorphous films, recent results depict preferred crystal orientation and even single crystalline nitride and oxide films obtained mainly by delicate substrate in-situ cleaning and careful plasma condition tuning and optimization.

In this talk, we will give an overview of the current state-of-the-art in PA-ALD research on wide and ultra-wide bandgap semiconductors, focusing mainly on wide bandgap III-nitrides (AlN, GaN) and III-oxides (Ga₂O₃). Subsequently, we'll share our recent research efforts on growing crystalline GaN and Ga₂O₃ thin films via PA-ALD utilizing two different plasma sources: inductively coupled plasma (ICP) and capacitively-coupled hollow-cathode plasma (CCHCP) source. We show that for III-nitride films, CCHCP source provides significant improvement in terms of oxygen impurity incorporation and structural film quality, while using a compact vacuum reactor with reduced source-to-substrate distance leads to reduced plasma power levels needed for self-limiting growth saturation curves. Both

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sources will also be compared in terms of film quality for ultra-wide bandgap Ga₂O₃.

We will present how the choice of plasma source and rf-plasma power affects the structural, chemical, optical, and electrical properties of the grown wide bandgap nitride and oxide films. Detailed x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), spectroscopic ellipsometer (SE), Hall measurements (HM) results and analyses will be presented. In addition to these ex-situ characterization results, we'll provide our real-time in-situ ellipsometric film growth monitoring results which provide valuable information about the single chemisorption, ligand-exchange/removal, and nitrogen/oxygen incorporation reactions.

We'll present proof-of-concept electronic and opto-electronic device demonstration based on GaN and Ga₂O₃ films grown via PA-ALD and will conclude with a future outlook in terms of how to further improve material quality and device performances.

5:00pm EM+OX+TF-TuA9 Wide Bandgap Dilute Magnetic Semiconductors for Room Temperature Spintronic Applications, V.G. Saravade, A. Ghods, Missouri University of Science and Technology, Rolla, MO, USA; N. Ben Sedrine, Universidade de Aveiro, Portugal; C. Zhou, Ian Ferguson, Missouri University of Science and Technology

INVITED

Wide bandgap dilute magnetic semiconductors (DMS) are promising materials for spintronic applications due to their theoretically predicted and experimentally observed ferromagnetic properties at room temperature (RT) [1]. Spintronics is an enabling technology for devices that will meet current and future computing needs through quantum computing, neuromorphic applications, and artificial intelligence.

Gallium nitride doped with rare earth or transition metals have exhibited ferromagnetic behavior for spintronic applications although its mechanism is still not well understood [1]. In order to build spin-based devices, it is necessary to understand, control, and manipulate their magnetic properties. MOCVD-grown GaGdN shows RT ferromagnetism as evidenced in vibrating sample magnetometry and anomalous Hall Effect (AHE) measurements. Also, AHE measurement showed that the mechanism for the ferromagnetism is intrinsic and likely mediated by free carriers, which is conducive for spintronic applications [2]. However, ferromagnetism is only observed with a Gd precursor, (TMHD)₃Gd, which contains oxygen in its organic ligand that appears to be incorporated into the GaGdN. As per density functional theory calculations, oxygen and carbon could introduce deep localized states close to the Fermi level in GaGdN that couple with Gd states to render ferromagnetism [3, 4]. To achieve a clarity and control of this phenomenon, O and C are intentionally implanted into GaGdN grown using oxygen-free Cp₃Gd source. In this case, as-grown GaGdN is not ferromagnetic, but post-implantation with O or C does result in ferromagnetism. X-ray diffraction exhibits low damage and good crystal quality for the implanted GaGdN with peak shifts as compared to the GaGdN before implantation, showing signs of O or C incorporation. Annealing the implanted GaGdN activates the dopant, improves the crystal quality, and shows clear signs of AHE. This indicates that the intrinsic and potentially free carrier-mediated RT ferromagnetism in GaGdN is activated by band states introduced by O or C. A better understanding of the mechanism for RT ferromagnetism will enable using these materials to build spintronic devices, and processors for high speed computing applications.

References

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5:40pm EM+OX+TF-TuA11 Processing and Characterization of Schottky and Ohmic contacts on (100) β-Ga₂O₃, Luke Lyle, K. Jiang, E. Favela, D. Moody, T. Lin, P. Chung, Carnegie Mellon University; K. Das, North Carolina State University; Z. Galazka, A. Popp, G. Wagner, Leibniz-Institut für Kristallzüchtung, Germany; L.M. Porter, Carnegie Mellon University

Over the past decade beta-gallium oxide (β-Ga₂O₃) has accrued increased interest due to its ultrawide bandgap of around 4.6 eV, superior figures of merit for numerous electronic and optoelectronic applications, and the

ability to produce single-crystal melt-grown substrates. Considering these factors, β-Ga₂O₃ has been primarily pursued for applications as high-power electronics, of which the understanding and development of Schottky and ohmic metal contacts is critical. In this study we characterized the electrical properties of electron-beam evaporated Ni, Mo, Au and other metal Schottky contacts to (100) β-Ga₂O₃ substrates. Prior to deposition of the metals, the Ga₂O₃ surface was cleaned via a 10% HCl solution followed by a clean in boiling 30% H₂O₂ solution at 85°C. Ti/Au was deposited via electron-beam evaporation and annealed at 400°C in an Ar atmosphere for use as ohmic contacts. The ideality factors, barrier heights, and doping densities were calculated from I-V and C-V measurements, which showed excellent agreement in most cases; I-V-T measurements are also planned as a complementary method to determine electrical transport behavior as a function of temperature. From our measurements it was observed that the Schottky barrier heights tended to increase as a function of the metal workfunction. These results are in contrast to our prior measurements of Schottky contacts on (-201) β-Ga₂O₃, which showed little to no correlation between Schottky barrier height and metal workfunction. In this presentation we will compare the electrical behavior of the various metal contacts on (100) β-Ga₂O₃, including the extracted ideality factors (~1.05–1.2) and Schottky barrier heights (~0.9–2 eV). The results will be discussed in the context of important processing conditions, as well as structural, optical, and morphological characteristics of (100) and (-201) β-Ga₂O₃ substrates as determined from x-ray diffraction, UV-visible spectroscopy, atomic force microscopy, and other techniques.

6:00pm EM+OX+TF-TuA12 III-Nitrides: Enabling Applications with Wide to Ultra-Wide Bandgap Materials and Devices, Erica Douglas, A.G. Baca, B.A. Klein, A.A. Allerman, A.M. Armstrong, A. Colon, C.A. Stephenson, R.J. Kaplar, Sandia National Laboratories

Though now commercially available, wide band gap semiconductors (WBG) such as GaN were pursued due to immense potential for high frequency, light-emission, and power electronic applications. Due to high breakdown voltages, which have been achieved due in part to intrinsic material properties and device engineering, as well as low on-state resistance, wide bandgap semiconductors have found significant success in the commercial application regime. The critical electric field that a material can withstand can be significantly increased through bandgap engineering due to critical field scaling as E_c^{2.5} [1]. Thus, moving from WBG materials with bandgaps ~3 eV, to UWBG with bandgaps above 3.4 eV, alloying GaN with Al can increase the bandgap from 3.4 eV (GaN) to 6.2 eV (AlN) and result in a critical electric field approaching 5X that of GaN.

Since the first AlGaN-channel transistor was reported in 2008 [2], development and progress on devices with increasing Al content has been pursued, including high electron mobility transistors with channel concentrations as high as 85% Al [3]. Though a corollary can be drawn to GaN, there are still a significant number of challenges to overcome for AlGaN-channel devices, ranging from epitaxial growth to fabrication. This talk will describe the latest results at Sandia National Laboratories in AlGaN-channel HEMTs, including recent advances in: enhancement-mode operation, current density, device performance over temperature, and RF operation.

This work was supported by the Laboratory Directed Research and Development program at Sandia National Laboratories. Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525.

- [1] R. J. Kaplar, *et al.*, *ECS J. Solid State Science and Technology*, vol. 6, p. Q3061 (2017).
- [2] T. Nanjo, *et al.*, *Appl. Phys. Lett.* **92**, 263502 (2008).
- [3] A.G. Baca, *et al.*, *Appl. Phys. Lett.* **109**, 033509 (2016).

Tuesday Afternoon, October 22, 2019

Complex Oxides: Fundamental Properties and Applications

Focus Topic

Room A220-221 - Session OX+EM+HC+MI+NS+SS+TF-TuA

Complex Oxides: Catalysis, Dielectric Properties and Memory Applications

Moderators: Alexander Demkov, University of Texas at Austin, Jeffrey Kelber, University of North Texas

2:20pm **OX+EM+HC+MI+NS+SS+TF-TuA1 Novel Multiferroic and Ferroelectric Ferrite Thin Films, Peter A. Dowben, C. Binek, X. Xu, University of Nebraska-Lincoln** **INVITED**

Ferroelectricity and ferromagnetism are foundational to numerous technologies, yet the combination of ferroelectricity and ferromagnetism, namely multiferroicity, may be even more desirable. Multiferroic materials are believed to be a route to voltage controlled spintronic devices. Yet very few single phase materials are known to be ferroelectric and ferromagnetic at the same time, i.e. multiferroic. Even fewer materials are fewer materials are magneto-electric, that is to say materials with magneto-electric coupling, i.e. voltage control of magnetization, but without separate order parameters for magnetism (or antiferromagnetism) and ferroelectricity. This talk will review the electronic structure of the tri-rutile magneto-electric antiferromagnets, like Fe_2TeO_6 , as well as rare earth ferrites like ReFeO_3 (Re = rare earth) stabilized in the hexagonal phase. Both types of materials are frequently antiferromagnetic, and, in principle, both can exhibit magneto-electric coupling. The surface termination affects the measured spin polarization of the surface and the interface with other materials. This will have a significant influence on the voltage control of magnetization. We have investigated the structural and electronic properties at the surface of these more unusual multiferroic materials using angle-resolved x-ray photoemission spectroscopy (ARXPS), complemented by x-ray diffraction (XRD), x-ray photoemission electron microscopy (X-PEEM), and X-ray circular dichroism. We find that the low local symmetry, especially at surfaces, will split the electronic states, via spin-orbit coupling. In some cases, the result is a net spin polarization at the surface, under electric field cooling. Because of the strongly preferential surface termination of these types of materials, the boundary polarization is roughness insensitive, in some cases making spintronic device applications plausible.

3:00pm **OX+EM+HC+MI+NS+SS+TF-TuA3 Potential Applications and Challenges for Complex Oxides in Advanced Memory and Computing Applications, Sebastian Engelmann, T. Ando, V. Narayanan, IBM T.J. Watson Research Center** **INVITED**

As the semiconductor industry continues to push for and develop higher performance computing systems, there is also a growing trend of redeveloping or optimizing fundamental computing approaches to be more energy efficient. The development of hardware for novel AI systems is no exception. New integration schemes, novel materials, multi-component materials or even nanoscale materials and the ability to integrate all of these approaches together becomes the compounded challenge. Deposition and etch technologies that offer differentiating solutions to these issues therefore need to meet somewhat conflicting demands, such as low damage processing as well as high rate processing beside many other issues.

Novel thin films, thin film laminates and alloys promising unprecedented performance are very interesting candidates to enable such computing paradigm shifts. In particular the class of complex oxides is a very interesting area of research as they offer new phenomena such as ferroelectricity, ferromagnetism or high temperature conductivity. While new phenomena are being discovered, unraveling the fundamental physics behind these properties is a critical element for an industrial exploitation of these properties.

In addition, these new and complex materials are growing the need for the ultimate process solution: atomic layer precision processing. Atomic layer etching is a promising path to answer the processing demands of new devices at the Angstrom scale. Self-limiting reactions, discrete reaction and activation steps or extremely low ion energy plasmas are some of the pathways being pursued for precise material removal control and maintaining the original film performance. Depending on the nature of the material, the etch response may be either too much or not enough chemical modifications of the material. Resulting modifications of the films is an important variable to consider in the readiness of material systems. In particular synergy to deposition approaches such as atomic layer deposition has been proposed as a solution, but more work is needed.

Tuesday Afternoon, October 22, 2019

4:20pm **OX+EM+HC+MI+NS+SS+TF-TuA7 Epitaxial Design of Complex Oxides for Catalysis and Electrocatalysis, Yingge Du, Pacific Northwest National Laboratory** **INVITED**

Predictive synthesis of highly active and cost-effective catalysts and electrocatalysts for energy conversion and storage is critical for leveraging intermittently available energy sources. Transition metal oxides with perovskite (ABO₃) and perovskite-related structures (e.g., Brownmillerite and Ruddlesden-Popper) have been identified as robust catalysts with high oxygen reduction reaction (ORR) and/or oxygen evolution reaction (OER) activities that rival the performance of noble metals and their compounds. The study of perovskites as epitaxial thin films enables measurement of their intrinsic catalytic activity, deconvolved from the effects of surface roughness and polycrystalline defects (e.g., grain boundaries and edges between facets). In addition, epitaxial growth facilitates accurate control over the composition, crystallographic orientation, and strain in thin films.

In this talk, our recent efforts in the design of epitaxial complex oxides for catalysis and electrocatalysis will be highlighted. Using LaNiO_3 , a bifunctional electrocatalyst, as an example, I will show how isovalent substitution, aliovalent substitution, and interfacial strain can be used to tune the structural, electronic, and optical properties of the resultant films, and how these observed changes correlate with their (electro)catalytic performance. The use of complex oxide thin films as support or anti-corrosion layers during catalytic reactions will also be discussed.

5:20pm **OX+EM+HC+MI+NS+SS+TF-TuA10 Vanadia/Tungsten Oxide on Anatase TiO₂(101): a Model Catalyst Study by STM and XPS, Tao Xu, J.V. Lauritsen, K.C. Adamsen, Aarhus University, Denmark; S. Wendt, iNANO, Aarhus University, Denmark**

Nitrogen oxides (NOX) from flue gas are in concern as major sources of air pollution. Increasingly stricter NOX emission control policies (e.g. Euro VI) demand innovation and better performance of NOX reduction technology. The Selective Catalytic Reduction (SCR) of NOX by vanadia supported on anatase titania, with tungsten oxide (WO₃) as promoter, has been widely used for this service and attracted much research attention. However, many aspects of the SCR catalysis process remain poorly understood at the atomic level. Particularly, the synergistic effect of tungsten oxide and vanadia remain elusive in literature, despite intensive RAMAN and infrared spectroscopy studies.

In this work, we use mineral α -TiO₂ single crystals exposing the (101) facets as the model surface and deposit V₂O₅ and WO₃ in our ultrahigh vacuum chamber (UHV) chamber by e-beam evaporation in oxygen. Combining Scanning Tunneling Microscope (STM) and X-ray photon-electron Spectroscopy (XPS), we systematically investigated the morphology and oxidation state changes of the model catalyst upon heating and reactant adsorption.

The STM results illustrate the distribution of V₂O₅ and WO₃ on anatase TiO₂(101) at the atomic level. It is found that both species are highly dispersed in the sub-monolayer region. For the deposition of surface oxide species, we explored different methods to achieve the highest oxidation state of vanadium (5+) and tungsten (6+). The thermal stability of the as-deposited V₂O₅ and WO₃ are investigated by XPS and STM systematically. We found that when V₂O₅ and WO₃ co-exist on the α -TiO₂ surface the stability of V₂O₅ is improved. This work provides atomic level understanding on the V₂O₅/WO₃/TiO₂ SCR catalyst and new insights into the synergistic interactions between vanadia and tungsten oxide on the α -TiO₂ surface.

5:40pm **OX+EM+HC+MI+NS+SS+TF-TuA11 Observation of Memory Effect and Fractal Surface in SrRuO₃ Epitaxial Thin Films, Ratnakar Palai, University of Puerto Rico; H. Huhtinen, University of Turku, Finland**

Integration of multifunctional oxide materials (ferroelectrics and multiferroics) into silicon technology is of great technological and scientific interests. The current interest in functional oxides is largely based on engineered epitaxial thin films because of their superior properties compared to the bulk and polycrystalline thin films and their technological applications in dynamic random access memories, magnetic recording, spintronics, and sensors. Most of these applications require bottom and top electrodes to exploit the electronic properties of the functional materials.

SrRuO₃ (SRO) has been found to be very useful for electrodes and junctions in microelectronic devices because of its good electrical and thermal conductivities, better surface stability, and high resistance to chemical corrosion, which could minimize interface electrochemical reactions, charge injection in oxide, and other detrimental processes, thus improving

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retention, fatigue resistance, and imprint. It also has good work function to produce the required large Schottky barrier on most ferroelectric oxide capacitors.

The bulk SRO exhibits several useful properties, such as extraordinary Hall effect, strong magnetocrystalline anisotropy, itinerant ferromagnetism, and spin-glass behavior. Spin-glass materials are currently frontier field of research and the most complex kind of condensed state of matter encountered so far in solid-state physics. Despite of the enormous importance of spin-glass models in neural networks, our knowledge of the underlying mechanistic processes involved is extremely limited. Although memory effect has been reported in bulk SRO, to our knowledge, the behavior is not well understood and there was no such report in thin films.

In this work, we report on the observation of memory effect and strong magnetic anisotropy in extremely smooth 1–3 Å roughness epitaxial (110) and (010) SrRuO₃ thin films. The observation of non-zero imaginary susceptibility and frequency dependent cusp at freezing temperatures confirms the spin-glass behavior, which agrees well with the dc magnetization measurement. The origin of memory effect can be attributed to the magnetic frustration and random interaction, which is affected by dynamics of cooling and will be discussed in details.

6:00pm **OX+EM+HC+MI+NS+SS+TF-TuA12 *In situ* Auger Electron Spectroscopy of Complex Oxide Thin Film Surfaces Grown by Pulsed Laser Deposition, Thomas Orvis, M. Surendran, Y. Liu, A. Cunniff, J. Ravichandran**, University of Southern California

Complex oxides can enhance the functionality of electronic and photonic devices by supplementing them with interesting properties such as ferroelectricity, superconductivity, and magnetoresistivity. Furthermore, low dimensionality in these materials can result in additional useful properties, inspiring the continued study of complex oxides in thin film form. However, the deposition of these materials is typically governed by notoriously complex growth mechanisms, revealing the need for *in situ* probes to observe and understand their precise nature. To this end, we report the *in situ* observation of chemical composition of complex oxide thin film surfaces with Auger electron microscopy during growth by pulsed laser deposition. Our implementation of real-time monitoring techniques for complex oxide thin films sheds an important light on the intricacies of the relationships between processing conditions and resulting composition.

Tuesday Evening Poster Sessions, October 22, 2019

Complex Oxides: Fundamental Properties and Applications Focus Topic

Room Union Station B - Session OX-TuP

Complex Oxides: Fundamental Properties and Applications Poster Session

OX-TuP1 Electrical and Structural Properties of p-type Transparent Conducting $\text{La}_{2/3}\text{Sr}_{1/3}\text{VO}_3$ Thin Films Grown Using RF Sputtering Deposition, D.H. Jung, Y.J. Oh, H.S. So, **Hosun Lee**, Kyung Hee University, Republic of Korea

The development of efficient p-type transparent conducting oxides (TCOs) remains a global material challenge. Converting oxides from n-type to p-type via acceptor doping is extremely difficult and these materials exhibit low conductivity due to the localized nature of the O 2p-derived valence band, which leads to difficulty in introducing shallow acceptors and small hole effective masses. High-quality perovskite oxide (ABO_3) thin film p-n junctions have significant potential for electronic devices with multifunctional properties. The p-type perovskites currently in use are not sufficiently transparent in the visible region. Alloying Sr and La at the A-sites of perovskite SrVO_3 , i.e. $\text{La}_{2/3}\text{Sr}_{1/3}\text{VO}_3$ (LSVO), can introduce holes at the top of the valence band (VB), resulting in p-type conductivity while maintaining reasonable transparency.

In this work, p-type LSVO thin films were grown on various substrates using RF magnetron co-sputtering deposition with SrVO_3 (actually $\text{Sr}_2\text{V}_2\text{O}_7$) and La_2O_3 targets between 400 and 500 °C with a mixed gas of H_2 (35%) and Ar. The generator powers were 60 and 30 W, respectively. Film thicknesses varied between 120 and 150 nm. The growth temperature and sputtering gas ambient were optimized and precisely controlled. The chamber pressure was set at . We used LSAT, LaAlO_3 , TiO_2/Si , Si, SiO_2/Si as substrates. The structural and morphological properties of LSVO films were studied using grazing angle incidence X-ray diffraction (GIXRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), spectroscopic ellipsometry, and X-ray photoemission spectroscopy (XPS). The electrical properties of all samples were measured using Keithley 4200. Hall effect measurements provided the Hall carrier concentration and Hall mobility as $3.0 \times 10^{20} \text{ cm}^{-3}$ and $5.15 \text{ cm}^2/(\text{V}\cdot\text{s})$, respectively. The resistivity was measured to be $4.1 \text{ m}\Omega\cdot\text{cm}$. In comparison, Hu et al. reported the resistivity, carrier concentration, and mobilities as $1.15 \text{ m}\Omega\cdot\text{cm}$, $1.69 \times 10^{21} \text{ cm}^{-3}$, and $3.2 \text{ cm}^2/(\text{V}\cdot\text{s})$, respectively for LSVO grown by using pulsed layer deposition [1]. GIXRD measurements showed $2\theta = 32.36^\circ$, which arose from (112) plane of tetragonal crystal structure of LSVO films. We discuss the substrate dependence of the electrical and optical properties of LSVO thin films in detail. We plan to develop all perovskite $\text{La}_{2/3}\text{Sr}_{1/3}\text{VO}_3/\text{SrVO}_3$ p-n junctions.

[1] L. Hu et al., Adv. Elect. Mater. **4**, 1700476 (2018).

OX-TuP2 van der Waals Heterostructures of Graphene and $\beta\text{-Ga}_2\text{O}_3$ Nanoflake for Enhancement Mode MESFETs and Logic Applications, Janghyuk Kim, J.H. Kim, Korea University, Republic of Korea

β -gallium oxide ($\beta\text{-Ga}_2\text{O}_3$) is a promising material for next-generation power electronics due to its wide band gap of $\sim 4.9 \text{ eV}$ and excellent productivity. Interestingly, a single crystalline $\beta\text{-Ga}_2\text{O}_3$ with a monoclinic structure can be exfoliated into ultra-thin flakes along the (100) plane due to its strong in-plane force and weak out-of-plane force. The exfoliated $\beta\text{-Ga}_2\text{O}_3$ flakes can be easily integrated with 2D materials (h-BN, TMDCs) to form van der Waals heterostructures for a down-scaled novel (opto)electronic devices as well. Most of the fabricated $\beta\text{-Ga}_2\text{O}_3$ transistors exhibit n-type characteristics with a negative threshold voltage (V_{th}) due to oxygen vacancy or donor like impurities in $\beta\text{-Ga}_2\text{O}_3$. The negative threshold voltage of n-type $\beta\text{-Ga}_2\text{O}_3$ transistors allows only a depletion mode (D-mode) operation, which limits their implementation in the circuit design. However, an enhancement mode (E-mode) operation, allowing simple circuit designs and fail-safe operation under high voltage conditions, is preferred for power transistors.

We have demonstrated a method to control V_{th} of $\beta\text{-Ga}_2\text{O}_3$ Metal-Semiconductor Field Effect Transistor (MESFET) by using various morphology of van der Waals heterostructure of $\beta\text{-Ga}_2\text{O}_3$ and graphene to achieve an E-mode operation. The junction of $\beta\text{-Ga}_2\text{O}_3$ and graphene forms a Schottky barrier due to the difference of their work functions. In the same $\beta\text{-Ga}_2\text{O}_3$ nanoflake, the $\beta\text{-Ga}_2\text{O}_3$ MESFET with a double gate of the sandwich structure of graphene/ $\beta\text{-Ga}_2\text{O}_3$ /graphene showed positive V_{th} (E-

mode operation) while the bottom gate only MESFET showed negative V_{th} (D-mode operation). Furthermore, a $\beta\text{-Ga}_2\text{O}_3$ /graphene van der Waals heterostructure based monolithic Direct Coupled FET Logic (DCFL) inverter was demonstrated by integrating E-mode and D-mode MESFETs on single $\beta\text{-Ga}_2\text{O}_3$ nanoflake and exhibited good inverter characteristics. These results show a great potential of van der Waals heterostructure of $\beta\text{-Ga}_2\text{O}_3$ /2D materials on future nanoscale smart power integrated circuit (IC) applications. The details of our results and discussions will be presented .

OX-TuP3 Structure and Reactivity of a Magnetite-Terminated Hematite Surface with Oxygen Adatoms Formed by Self-Oxidation, Constantin Walenta, F. Xu, W. Chen, C.R. O'Connor, C.M. Friend, Harvard University

The surface composition and structure of reducible oxides, including oxides of Fe, are complex and difficult to control because of the mobility and multiple oxidation states of cations. The magnetite phase of iron oxide is a material with a complex structure and controversial surface terminations that is widely used in heterogeneous catalysis, including the water gas shift reaction and formaldehyde synthesis.

A new, unique termination of oxygen adatoms forms on top of $\text{Fe}_3\text{O}_4(111)$ film on a $\alpha\text{-Fe}_2\text{O}_3(0001)$ single crystal in oxygen-deficient environments. By using a combination of chemical and activity analysis (XPS and TPRS), structure analysis (STM and LEED) and DFT calculations, we identify the atomic structure of the as-prepared $\text{Fe}_3\text{O}_4(111)$ surface and distinguish electronic structure of oxygen adatom and uncovered iron sites. The latter is an active Lewis site for alcohol dissociation at room temperature. Further oxidation of the alkoxy intermediate to the aldehyde occurs at 700 K, and the surface fully recovers after product desorption.

The work establishes a clear understanding of a unique magnetite surface and provides insights in the selective oxidation of alcohols on iron oxide-based catalysts and a rare direct observation of oxygen mobility in iron-oxide based materials.

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 $(\text{LFO}_z/\text{SNO}_1)_{21}$ 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 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 SNT0, along with surface depletion. We have probed these buried interfaces using hard x-ray

¹ Medard W. Welch Award Winner

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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.

Acknowledgement: Work at UNL was supported in part by the Semiconductor Research Corporation (SRC) as task 2760.002 and NSF through ECCS 1740136.

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.

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic

Room A213 - Session HC+OX+SS-WeA

Metal-Support Interactions Driving Heterogeneously-Catalyzed Reactions

Moderators: Aravind Asthagiri, The Ohio State University, Jason Weaver, University of Florida

2:20pm **HC+OX+SS-WeA1 Yttria-stabilized Zirconia (YSZ) Supports for Low Temperature Ammonia Synthesis**, Z. Zhang, S. Livingston, Colorado School of Mines; L. Fitzgerald, University College Dublin; J.D. Way, Colin Wolden, Colorado School of Mines

The use of renewable hydrogen for distributed synthesis of ammonia requires the development of efficient catalysts and processes that operate under mild conditions. Here we introduce yttria stabilized zirconia (YSZ) as a more active Ru catalyst support for NH_3 synthesis than traditionally used supports such as Al_2O_3 . The addition of Cs promoter increased rates an order of magnitude higher by reducing the apparent activation energy from 103 kJ/mol to 65 kJ/mol. The rate enhancement is largely insensitive to the amount of promoter addition, with Cs outperforming Ba and K by a factor of 2. At 400°C under 1.0 MPa, the synthesis rate was comparable with that of most active oxide-supported Ru catalysts. The rate becomes inhibited by H_2 adsorption at low temperature (< 350°C), but the use of lower H_2/N_2 ratios enables the rate to remain comparable to what is observed in stoichiometric mixtures at temperatures > 400°C. A detailed microkinetic model was developed that successfully captures the observed behavior, revealing that adsorption is coverage dependent. These results provide insight and direction into developing alternatives to Haber-Bosch for distributed synthesis of green ammonia.

2:40pm **HC+OX+SS-WeA2 Operando PTRF-XAFS Technique for 3D Structure Determination of Active Metal Sites on a Model Catalyst Surface under Working Conditions**, Satoru Takakusagi, L. Bang, D. Kido, Y. Sato, K. Asakura, Hokkaido University, Japan

Polarization-dependent total reflection fluorescence (PTRF)-XAFS is a powerful technique which can determine 3D structure of highly dispersed metal species on a single-crystal surface by measuring polarization-dependent XAFS of the metal species. To obtain atomic-level understanding of metal/oxide-support interaction in heterogeneous catalysis, we have determined the precise 3D structures of single metal atoms and metal clusters deposited on single-crystal oxide surfaces such as $\text{TiO}_2(110)$ and $\text{Al}_2\text{O}_3(0001)$ by UHV PTRF-XAFS apparatus.^[1]

Recently we have constructed a new apparatus which enables us to measure PTRF-XAFS of active metal species dispersed on a single-crystal oxide surface under working condition. A compact vacuum chamber which works both as PTRF-XAFS cell and batch-type reactor was designed and constructed. The sample can be transferred without exposure to air from another UHV chamber where the sample preparation (ion sputtering, annealing and metal deposition) and its surface characterization (LEED, XPS) are carried out. The sample in the compact chamber can be heated at high temperatures (< 700 °C) in the presence of reactant gases (typically 10~100 Pa), which makes the operando PTRF-XAFS measurements possible. Thus 3D structure-activity relationship of the active metal species on an oxide surface in heterogeneous catalysis can be obtained. We will show the details of the operando PTRF-XAFS technique and its application to CO oxidation on a $\text{Pt}/\text{Al}_2\text{O}_3(0001)$ surface.

(References)

[1] S. Takakusagi et al., *Chem. Rec.* **18** (2018) 1, *J. Phys. Chem. C* **120** (2016) 15785, *Top. Catal.* **56**(2013) 1477, *Phys. Chem. Chem. Phys.* **15**(2013) 14080.

3:00pm **HC+OX+SS-WeA3 Understanding and Tuning Catalytic Materials Using Nanocrystal Precursors**, Matteo Cargnello, Stanford University
INVITED

Catalytic processes are central to the goal of a sustainable future. A promising approach in developing catalytic materials is represented by the design of catalytic sites based on the knowledge of reaction mechanisms and structure-property relationships and aided by computation, and in the precise synthesis of these sites at the atomic and molecular level. The materials-pressure gap, however, still hinders the full realization of this strategy. Nanocrystal precursors, with tunable active sites and compositions, can help bridge this gap. The goal of this talk is to show how

this approach can provide not only fundamental understanding of catalytic reactions, but also represents a way to precisely engineer catalytic sites and metal-support interactions to produce efficient catalysts that are active, stable and selective for several important catalytic transformations. Examples of the use of these building blocks as supported systems or in combination with hybrid organic materials will be shown, both to understand trends in methane and CO_2 activation, and in the preparation of optimized catalytic systems combining multiple active phases. In all these examples, important efforts to obtain useful structure-property relationships will be highlighted, with this knowledge used to prepare more efficient catalysts for sustainable production of fuels and chemicals.

4:20pm **HC+OX+SS-WeA7 CO_2 Hydrogenation on Supported Zirconium Oxide Clusters**, Yilin Ma¹, Stony Brook University; M.G. White, Brookhaven National Laboratory

In this work, zirconium atoms and zirconium oxide clusters are deposited onto metal/metal oxide surfaces as model “inverse” catalysts for the study of CO_2 hydrogenation. The control over the stoichiometry of clusters and the oxidation state of the metal centers enables the study of atomic level details such as identification of active sites, interfacial electron transfer and the role of sulfur vacancies. Recent AP-XPS, AP-IR and STM results of supported zirconium oxide on $\text{Cu}_2\text{O}/\text{Cu}(111)$ surface will be presented. Reactivity studies over $\text{Zr}/\text{Cu}_2\text{O}/\text{Cu}(111)$ show that the formation of $\text{CO}_2^-(\text{ad})$ and HCOO^- can be seen on regions with the presence of Zr on Cu_2O surface during the reaction condition ($\text{CO}_2/\text{H}_2=1$, total pressure=0.5torr), however CO_2 only binds weakly on bare $\text{Cu}_2\text{O}/\text{Cu}(111)$ surface. Moreover, the change of zirconium oxidation state indicates the adsorption of CO_2 happens on metal or metal-support interface, where the zirconium gets oxidized when exposing to CO_2 . Some DFT studies of above systems will also be shown, including the electronic structures of clusters, binding sites of CO_2 molecules, etc.

4:40pm **HC+OX+SS-WeA8 Tuning Surface Hydrophobicity to Enhance Reaction Rate of the Lewis Acid Zeolite Nano Sn Beta for Alcohol Ring Opening of Epoxides**, Nicholas Brunelli, A.P. Spanos, A. Parulkar, N. Deshpande, The Ohio State University

Ring opening epoxides produces compounds that are valuable in the production of fine chemicals and pharmaceuticals. Recent work¹ has demonstrated that the bulky reactants typically involved in fine chemical synthesis benefit from reducing the length scale of the materials to produce nano-zeolites (nano-Sn-Beta), which requires using a custom-synthesized structure directing agent in hydroxide conditions. While the nanozeolites can achieve higher overall conversion than Sn-Beta synthesized using fluoride conditions, the initial reaction rate is higher for Sn-Beta that tends to be hydrophobic compared to nano-Sn-Beta that is demonstrated to be hydrophilic. These results suggest that the alcohol ring opening reaction is sensitive to the reaction environment. The surface of nano-Sn-Beta can be treated to reduce the amount of defects and correspondingly increase the hydrophobicity. Interestingly, the treatment of nano-Sn-Beta materials more than doubles the observed reaction rate. Overall, this demonstrates a valuable method to tune the reaction environment that could be widely applicable to many chemical reactions.

References

(1) Parulkar, A.; Spanos, A. P.; Deshpande, N.; Brunelli, N. A. Synthesis and catalytic testing of Lewis acidic nano zeolite Beta for epoxide ring opening with alcohols. *Applied Catalysis A: General*, **2019**, 577, 28–34.

5:00pm **HC+OX+SS-WeA9 Understanding Metal-Metal and Metal-Support Interactions in Bimetallic Catalysts**, Donna Chen, University of South Carolina; S. Farzandh, D.M. Shakyia, A.J. Brandt, T.D. Maddumapatibandhi, University of South Carolina
INVITED

Bimetallic catalysts are known to exhibit superior properties compared to their individual pure metal components, but in many cases the nature of these improved properties is not well understood. The main goal of this work is to understand how oxidation states, metal-support interactions, and metal-metal interactions in supported bimetallic clusters can be used to control catalytic activity. Specific catalytic reactions investigated are the water gas shift reaction (WGS) on Pt-Re and selective hydrogenation of unsaturated aldehydes on Pt-Sn. Model catalyst surfaces are prepared via vapor-deposition of metal clusters on single-crystal oxide and carbon supports. These surfaces are fully characterized by a variety of ultrahigh vacuum (UHV) surface science techniques and their activities are studied in a microreactor ($P \sim 1$ atm) coupled to the UHV chamber. Scanning tunneling

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microscopy investigations indicate that exclusively bimetallic clusters can be prepared by sequential deposition of metals. For the WGS reaction, the active site is determined to be Pt with subsurface Re, while Re oxide does not play a role. Density functional theory studies show that the presence of subsurface Re decreases the adsorption energy of CO on Pt, thus preventing Pt active sites from being poisoned by CO. WGS activity increases with increasing perimeter for Pt/TiO₂ clusters, and the turnover frequency is also lower in the absence of the TiO₂ support. For hydrogenation on furfural, the Pt-Sn alloy surface exhibits high selectivity to furfuryl alcohol compared to pure Pt, whereas furan and tetrahydrofuran are the main products on Pt.

Surface Science Division

Room A220-221 - Session SS+AS+HC+OX-WeA

Reactions at Alloy Surfaces and Single Atom Catalysis

Moderators: Erin Iski, University of Tulsa, Bruce E. Koel, Princeton University

2:20pm SS+AS+HC+OX-WeA1 Correlating Structure and Function for Nanoparticle Catalysts, *Graeme Henkelman*, University of Texas at Austin INVITED

Metal nanoparticles of only 100-200 atoms are synthesized using a dendrimer encapsulation technique to facilitate a direct comparison with density functional theory (DFT) calculations in terms of both structure and catalytic function. Structural characterization is done using electron microscopy, x-ray scattering, and electrochemical methods. Combining these tools with DFT calculations is found to improve the quality of the structural models. DFT is also successfully used to predict trends between structure and composition of the nanoparticles and their catalytic function for reactions including the reduction of oxygen and selective hydrogenation. This investigation demonstrates some remarkable properties of the nanoparticles, including facile structural rearrangements and nanoscale tuning parameters which can be used to optimize catalytic rates. In this presentation I will focus on a pair of random alloy bimetallic nanoparticles which have complete different trends in hydrogenation activity as a function of composition. Pd/Au is found to be tunable as a function of composition whereas Pt/Au is not. The reason behind these different behaviors will be discussed.

3:00pm SS+AS+HC+OX-WeA3 Surface Reactivity of PtAg and PdAg: From Single-Atom Alloys to Supported Nanoparticles, *Dipna Patel*^{1,2}, Tufts University; *C.R. O'Connor, R.J. Madix, C.M. Friend*, Harvard University; *E.C.H. Sykes*, Tufts University

Catalytic hydrogenation reactions are important in many industrial applications. While Pt and Pd are catalytically active towards hydrogenation, they are often costly, and can suffer from poisoning by CO and coke. Previously, Ag based catalysts have been modified by alloying Pt or Pd for applications in highly selective heterogeneous catalysis. This has shown promise for catalyst design since Ag is cheaper and more resilient to poisoning. It is well known that ensemble size can dramatically change the catalytic pathway, however the atomic-scale structure of PtAg and PdAg alloys and their relation to catalytic activity is still unknown. Using scanning tunneling microscopy (STM) and STM-based spectroscopies, we characterized the surface structure and local geometry of Pt deposited on Ag(111) as a function of alloying temperature. At low temperatures, intermixing of PtAg is driven by a negative mixing enthalpy, resulting in different metastable states such as isolated Pt atoms in, and islands on, Ag terraces, as well as Pt rich brims located along Ag step edges. Increasing the alloying temperature results in an increased concentration of Pt atoms along Ag steps edges as well as direct exchange of Pt atoms into Ag terraces. At higher temperatures, there is sufficient thermal energy for Pt atoms to fully disperse in the Ag(111) surface layer as isolated atoms, forming single-atom alloys. STM characterization of the surface structure of PdAg alloys reveals the formation of large Pd islands on Ag(111). Using STM, we investigated H₂ activation on active Pd sites and spillover on to Ag(111). The characterization of PtAg and PdAg surface alloys enables us to correlate reaction activity and selectivity to the atomic-scale structure of the alloy and to inform catalyst design that optimizes catalytic selectivity.

3:20pm SS+AS+HC+OX-WeA4 Single-site Catalysts by Metal-ligand Complexation at Surfaces: From Model Systems in Vacuum to High-pressure Catalysis on Oxide Supports, *Steven L. Tait*, Indiana University

A grand challenge in heterogeneous catalysis is to achieve high levels of selectivity by controlling the chemical uniformity of metal catalyst sites at surfaces. Our group is working to apply principles of on-surface metal-organic redox assembly to develop a new approach to this problem. Metal-organic coordination networks at surfaces hold promise for selective chemical function, but there is a limited understanding of the chemical reactivity of these systems. Studies of model systems in ultra-high vacuum allow for detailed characterization of the structure and chemistry of these systems. We tested chemical activity of vanadium single-site complexes that are stabilized by tetrazine-based ligands and found activity toward dioxygen activation with a high degree of selectivity compared to vanadium nanoparticles. Reaction with O₂ causes an increase in V oxidation state from V^{III} to V^{IV}, resulting in a single strongly bonded V-oxo product and spillover of O to the Au surface [1]. The metal centers are stabilized in extended, ordered metal-organic complexes that self-assemble through an on-surface redox process on the Au(100) surface and are characterized by X-ray photoelectron spectroscopy, scanning tunneling microscopy, high-resolution electron energy loss spectroscopy, and density functional theory. New results extend these chemical studies to more complex systems that include bimetallic sites and redox isomer systems [2-3], which will also be highlighted in this presentation.

We have also developed synthesis schemes to assemble quasi-square planar metal-organic complexes on high surface area powdered oxides under ambient conditions through a modified wet-impregnation method. X-ray photoelectron spectroscopy measurements demonstrate loading of metal and ligand on the surface and synchrotron-based X-ray absorption spectroscopy measurements of the coordination shell of the metal centers demonstrates single site formation rather than nanoparticle assembly [4-5]. These systems are shown to be active for the catalysis of hydrosilylation reactions at a level that is competitive with current homogeneous catalysts. They also show excellent activity for hydrogenation in flow reactor experiment.

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3. Morris, Huerfano, Wang, *et al.*, *Chem. Eur. J.*, **25**, 5565-5573 (2019). DOI: 10.1002/chem.201900002

4. Chen, Sterbinsky, and Tait, *J. Catal.*, **365**, 303-312 (2018). DOI: 10.1016/j.jcat.2018.07.004

5. Chen, Ali, Sterbinsky, *et al.*, *ChemCatChem*, *in press* (2019). DOI: 10.1002/cctc.201900530

4:20pm SS+AS+HC+OX-WeA7 Controlling the Local Coordination and Reactivity of Oxide-supported Atomically Dispersed Pt-group Species, *Phillip Christopher*, University of California at Santa Barbara INVITED

The synthesis of oxide supported Pt-group catalysts typically produces metal particles with dimensions of a few nanometers. Recent work has shown that Pt-group species can co-exist as nanoparticles and single atoms, and that careful synthetic approaches can produce exclusively single atoms. Interest in the reactivity of supported isolated Pt-group metal atoms stems from the maximized metal utilization efficiency, unique reactivity or selectivity, connection to organometallic catalysis, and the potential for making well-defined active sites. It has proven challenging to characterize the intrinsic catalytic activity of these dispersed active sites on oxide supports at a level that relates local electronic and geometric structure to function. The difficulty arises from their atomic dispersion, heterogeneity in the local coordination of active sites on most catalysts (i.e. isolated species sit at different sites on the support), dynamic changes in local coordination under reactive environments, and often the low loading of metal that is required to achieve site isolation.

In this talk I will describe a synthetic approach to produce isolated Pt-group atoms that exhibit uniformity in their bonding environment on an oxide support and show how a combination of microscopy, spectroscopy and theory can be used to describe the local coordination of these species. Then I will describe two different approaches to control the local environment of Pt-group atoms: (1) through varied pre-treatment that tunes the local coordination and oxidation state of the single atom, and (2) through the site selective deposition of single atoms near well-defined acid sites on oxide supports. Detailed characterization by a combination of

¹ Morton S. Traum Award Finalist

² National Student Award Finalist

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spectroscopy and microscopy is used to develop structure-function relationships for these well-defined single atom active sites in the context of CO oxidation, methanol carbonylation and ethylene hydroformylation. This work highlights the ability to tune the local environment of single Pt-group atom active sites on oxide supports in analogous ways to the engineering of organometallic catalysts.

5:00pm **SS+AS+HC+OX-WeA9 Coordination Defines Reactivity of a Model Single-atom Catalyst: Ir₁/Fe₃O₄(001)**, Zdenek Jakub¹, J. Hulva, M. Meier, U. Diebold, G.S. Parkinson, TU Wien, Austria

The development of single-atom catalysts (SACs) was originally motivated by saving of the precious metal, but an equally intriguing characteristic of the ideal SAC is potentially high selectivity due to the high number of identical active sites. The coordination of the active metal center is known to play a crucial role in homogeneous catalysis, and in this talk, I will demonstrate that similar effects can be observed on a model single atom catalyst: Ir₁/Fe₃O₄(001). Using scanning tunneling microscopy (STM), noncontact atomic force microscopy (nc-AFM), temperature programmed desorption (TPD), x-ray photoemission spectroscopy (XPS) and DFT calculations, I will show that the coordination of single Ir₁ adatoms can vary depending on preparation, and that the local environment has dramatic consequences for the ability of the catalyst to adsorb CO. As deposited at room temperature, Ir atoms take 2-fold coordination to the surface oxygen atoms. Upon annealing, they incorporate into the first surface layer (5-fold coordinated Ir₁), and then into the first subsurface layer (6-fold coordinated Ir₁). The 2-fold adatoms can form both monocarbonyls and dicarbonyls, but the 5-fold Ir only binds a single CO. The structures are understood by analogy to square planar Ir(I) and octahedral Ir(III) complexes, respectively. The 6-fold Ir is coordinatively saturated, and thus deactivated for CO adsorption. These results show that control of the local coordination environment is critical to design so-called single-atom catalysts, and that incorporation into the support can be as critical a deactivation mechanism as thermal sintering.

5:20pm **SS+AS+HC+OX-WeA10 Capturing the Early Stages of Oxidation on Low-Index Ni and Ni-Cr Surfaces**, William H. Blades, P. Reinke, University of Virginia

The early stages of oxidation and corrosion of alloys control the structure and development of the oxide layer and therefore decisively influence its protective function. To this end, we have studied the nanoscale evolution of surface oxides prior to the formation of a complete layer. The oxidation of Ni(100), Ni(111), and Ni-Cr(100), Ni-Cr(111) surfaces was captured by sequential oxidization and measured with scanning tunneling microscopy/spectroscopy (STM/STS). The early-stage oxidation, and the influence of alloy composition and crystallographic orientation on surface reactivity, was studied by comparing pure Ni(100/111) and Ni-Cr(100/111) surfaces. Alloy thin films (8-18 wt.% Cr) were prepared on MgO(100/111) and exposed to oxygen up to 400 L at 773 K. Under these conditions, oxide nucleation is predicated by the development of oxygen adlayers on both the pure Ni(100/111) surfaces. The formation of a c(2x2)-O chemisorbed phase on the Ni(100) surface causes the step edges to facet into {100} segments, kinetically limiting NiO growth. However, no such faceting is observed on the Ni(111) surface and the nucleation and growth of NiO begins after only 300 L of O₂. Our experiments demonstrate that the addition of small amounts of Cr completely change the oxidation pathways. On the Ni-Cr(100) surface, the nucleation and growth of NiO initiates along the step edges, forming low-angle NiO wedges with a NiO-Ni(7x8) superstructure. Terrace oxide growth commences with the nucleation of small oxide particles, driven by the presence of Cr, which grow into large oxide nodules after further oxidation. NiO growth extends into the terraces and takes a NiO-Ni(6x7) cube-on-cube interfacial relationship. Several novel surface reconstructions are observed and are tentatively attributed to Cr(100)-O reconstructions, suggesting surface segregation and phase separation of BCC Cr. Similarly, nano-sized oxide particles nucleate on the Ni-Cr(111) terrace and step edges, while single atomic NiO rows extend across the surface. Oxide nodules, similar to those found on the Ni-Cr(100) surface are observed and grow laterally along the terraces. Each of these aforementioned surface oxides present unique electronic signatures, and STS maps are used to quantify the spatial variations in their density of states and band gaps. The electronic heterogeneity of the surface underscores that the use of a homogenous electric field to capture oxidation kinetics at the alloy-oxide interface should be revisited.

5:40pm **SS+AS+HC+OX-WeA11 Evolution of Steady-state Material Properties during Catalysis: Oxidative Coupling of Methanol over Nanoporous Ag_{0.03}Au_{0.97}**, Matthijs van Spronsen, Lawrence Berkeley National Laboratory; B. Zugic, Harvard University; M.B. Salmeron, Lawrence Berkeley National Laboratory; C.M. Friend, Harvard University

Activating pretreatments can be used to tune both surface composition and surface structure of bimetallic alloy catalysts. Careful selection of both gas mixtures and reaction temperatures can lead to surfaces that are able to achieve optimum selectivity and activity under steady-state reaction conditions. The activation-induced changes in material properties of a nanoporous (np) Ag_{0.03}Au_{0.97} alloy and their subsequent evolution under steady-state conditions for CH₃OH oxidation are presented. Initial activation by oxidation in O₃ at 423 K leads to the formation of AgO and Au₂O₃ driving a strong Ag enrichment in the near-surface region, based on ambient-pressure X-ray photoelectron spectroscopy (AP XPS) and extended X-ray absorption fine structure (EXAFS) analysis. Exposing this oxidized np Ag_{0.03}Au_{0.97} to the O₂/CH₃OH reaction mixture reduces both Ag and Au oxides and results in a surface alloy locally highly enriched in Ag. Both the oxides and the highly Ag enriched alloy unselectively oxidize methanol to CO₂. However, at the reaction temperature of 423 K, the Ag slowly realloys with Au. Although decreasing, the composition remains enriched in Ag in the top few nanometers under steady-state conditions. The Ag content in the surface is 29 at.% in steady state and the desired product, methyl formate, is selectively produced without significant deactivation. The activation and evolution of the active phase is not uniform: nanometer-scale patches of AgO, leading locally to Ag-rich alloys, were observed with environmental transmission electron microscopy (E TEM). These local Ag-rich AgAu alloy regions are critical for initiation of the catalytic cycle through O₂ dissociation. Calculations based on density-functional theory (DFT) indicate that the O on the surface assist in stabilizing the Ag. Moreover, an essential factor for retaining this local enrichment in Ag is the modest reaction temperature of 423 K. At higher temperatures, bulk diffusion induces sintering and redistribution of the Ag, leading to a loss of activity. These findings demonstrate that material properties determining catalytic activity are *dynamic* and that metastable (kinetically trapped) forms of the material may be responsible for catalysis. Hence, catalytic activity and selectivity depend on the pretreatment, reaction temperature and gas composition. These observations provide guiding principles concerning the activation of heterogeneous catalysts for selective oxidation.

6:00pm **SS+AS+HC+OX-WeA12 Reduction and Oxidation of Transition Metal Oxides: From Tailoring the Surface and Interface Properties to the New Crystalline Phases Formation**, Dominik Wrana, Jagiellonian University, Poland; C. Rodenbücher, Forschungszentrum Jülich GmbH, Germany; K. Ciešlik, B.R. Jany, Jagiellonian University, Poland; K. Szot, Forschungszentrum Jülich GmbH, Germany; F. Krok, Jagiellonian University, Poland

In the recent years transition metal oxides have attracted tremendous interest, mostly due to the manifold real applications, ranging from (photo)catalysis, through memristive and neuromorphic device development, to energy storage and production. A specific quality which makes them so versatile is the ease by which their electronic and structural properties can be controlled by changing a cation's reduction state.

In this presentation we will present an overview of the impact that thermal reduction and oxidation have on the surface properties, which enable a precise control over the valence state of prototypical binary and ternary oxide representatives: TiO₂ and SrTiO₃. We will focus on the preparation methods under regular UHV conditions and upon additionally reduced oxygen partial pressure.

Reduction of both crystals results in the formation of oxygen vacancies and therefore d-electrons, which leads to changes in the work function and a corresponding rise in electrical conductivity, which could be tuned over many orders of magnitude [1]. A newly developed SPM-based technique, combining LC-AFM and KPFM, allows both measurements to probe the same area of the reduced TiO₂(110) surface [2], helping understanding of the nanoscale resistive switching. Besides the change in electrical properties, the surface structure evolves towards nonstoichiometric reconstructions [1], due to the increased oxygen deficiency. Surprisingly, not only is oxygen flow possible during UHV annealing of the oxide crystal, but also incongruent cation sublimation can be triggered, as demonstrated for the perovskite oxides like SrTiO₃ [3]. Extremely low oxygen partial pressure (ELOP), achieved by the use of an oxygen-getter, initiates SrTiO₃ crystal decomposition and the formation of stable monocrystalline cubic TiO nanowires with a c(4x4) reconstructed surface [4]. Such bottom-up

¹ Morton S. Traum Award Finalist

Wednesday Afternoon, October 23, 2019

growth of conductive TiO nanostructures could be an alternative to other costly methods, resulting in the creation of the TiO/SrTiO₃ interface, with a sharp transition between Ti²⁺ and Ti⁴⁺ states, proven by atomically-resolved electron microscopy. This oxide heterostructure provides an interesting metal/insulator junction with a 0.6 eV work function difference [5], opening many new possibilities for (photo)catalysis and aiding in the search for exotic interface states.

[1] Wrana, D. et al. (2018) *Applied Surface Science*, 432, 46-52.

[2] Rodenbücher, C. et al. (2018) *APL Materials*, 6(6), 066105.

[3] Rodenbücher, C. et al. (2017) *physica status solidi (RRL)–Rapid Research Letters*, 11(9), 1700222.

[4] Wrana, D. et al. (2019) *Nanoscale*, 11(1), 89-97.

[5] Wrana, D. et al. (2019) *Beilstein Arch.*, 201912.

Surface Science Division

Room A220-221 - Session SS+2D+AP+AS+OX+SE-ThA

Dynamics at Surfaces/Reactions and Imaging of Oxide Surfaces

Moderators: Irene Groot, Leiden University, The Netherlands, William E. Kaden, University of Central Florida

2:20pm SS+2D+AP+AS+OX+SE-ThA1 Adsorption, Reaction, and Diffusion of Energetic Reagents on Morphologically Diverse Thin Films, *Rebecca Thompson*^{1,2}, *M.R. Brann, S.J. Sibener*, The University of Chicago

I present work from two studies illustrating the impact of condensed-phase film morphology on reaction kinetics and surface adsorption. To begin, I will discuss the **oxidative reactivity of condensed propene films**. This work is conducted in a state-of-the-art ultra-high vacuum chamber equipped for operation at cryogenic substrate temperatures. Time-resolved reflection absorption infrared spectroscopy (RAIRS) is used to track propene reactivity when films are exposed to a supersonic expansion of ground state oxygen atoms, O(³P). I demonstrate that propene reacts significantly on exposure, producing primarily propylene oxide and propanal. Oxide production is significant; partial oxidation products are rarely observed in gas phase studies and olefin oxides are incredibly important chemical intermediates in a variety of industrial processes. Regardless of initial film thickness, the reaction follows zero order kinetics, with a calculated activation energy of 0.5 kcal mol⁻¹. This low barrier closely matches that reported in gas phase studies, suggesting that the condensed-phase reaction is likely diffusion-limited. I also highlight that the propene deposition temperature has a substantial impact on reactivity. Films deposited below 50 K produce dramatically different RAIR spectra that correspond to a more amorphous film composition. These films are nearly unreactive with O(³P), indicating that oxygen diffusion is directly tied to the density and ordering in the more crystalline film.

This dependence on film structure is also observed in the second study, which explores **embedding in and adsorption on crystalline, non-porous amorphous, and porous-amorphous water ice films**. Using a combination of supersonic molecular beams, RAIRS and King and Wells mass spectrometry techniques, I demonstrate that direct embedding into the bulk is remarkably insensitive to film structure; the momentum barrier is identical between amorphous and porous-amorphous ice films. Below this barrier, however, sticking probabilities differ considerably between the different films, suggesting that the pore structure is more efficient at dissipating incident energy. These discoveries are critical for the accurate quantitative modeling of molecular uptake and reactivity on icy astrophysical bodies such as comets and planetesimals. When taken together, these two studies provide fundamental mechanistic insight into the sticking, diffusion, and reactivity of small molecules on complex films, with a specific emphasis on the impact of film morphology and organization.

2:40pm SS+2D+AP+AS+OX+SE-ThA2 Oxidation of Semiconductors and Semimetals by Supersonic Beams of O₂ with Scanning Tunneling Microscopy Visualization, *Ross Edel*³, *T. Grabnic, B. Wiggins, S.J. Sibener*, The University of Chicago

Our research examines the oxidation of semiconductor and semimetal surfaces using a novel, one-of-a-kind instrument that combines a supersonic molecular beam with an in-line scanning tunneling microscope (STM) in ultra-high vacuum. This new approach to surface reaction dynamics provides spatiotemporal information on surface oxidation over nanoscopic and mesoscopic length scales. We have uncovered the kinetic and morphological effects of oxidation conditions on three technologically relevant surfaces: Si(111)-7×7, highly oriented pyrolytic graphite (HOPG), and GaAs(110). A complete understanding of the oxidation mechanism of these surfaces is critical due to their technological applications and roles as model systems. Samples were exposed to O₂ with kinetic energies from 0.4-1.2 eV and impingement angles 0-45° from normal, with STM characterization between exposures. In some cases, we were able to monitor the evolution of specific features by revisiting the same nanoscopic locations. Our study of Si(111)-7×7 revealed two oxidation channels, leading to the formation of dark and bright reacted sites. The

dark sites dominated the surface and exhibited almost no site selectivity while the bright sites preferred the corner sites of the 7×7 unit cell. Our observations suggest that two adsorption pathways, trapping-mediated and direct chemisorption, occur simultaneously. On HOPG, we found that different oxygen energies, incident angles, and surface temperatures produce morphologically distinct etching features: Anisotropic channels, circular pits, and hexagonal pits. Reaction probability increased with beam energy and demonstrated non-Arrhenius behavior with respect to surface temperature, peaking at around 1375 K. Finally, oxidation of GaAs(110) was found to proceed by two morphologically distinct, competing mechanisms: a homogeneous process leading to layer-by-layer oxide growth, and a heterogeneous process with oxide islands nucleating from surface defects. The rates of both mechanisms change with O₂ kinetic energy, with homogeneous oxidation dominating at lower energies (<0.7 eV) and heterogeneous oxidation with higher energies (≥1.0 eV). The results obtained in this work provide vital information about the morphological evolution and kinetics of semiconductor and semimetals, offering a comprehensive overview of the spatiotemporal correlations that govern oxidation dynamics on surfaces.

3:00pm SS+2D+AP+AS+OX+SE-ThA3 Studying Molecule-Surface Interactions using Rotational Orientation Control of Ground-State Molecular Beams, *Gil Alexandrowicz*, Swansea University, UK INVITED

Performing quantum state selective experiments of molecule-surface collisions provides unique insight into the interaction potential. One particularly tricky molecular property to control and measure is the rotational projection states, i.e. the orientation of the rotational plane of the molecule. Previous data was mostly restricted to photo-excited/paramagnetic species. In this talk, I will describe the molecular beam apparatus which allows to control and measure the rotational orientation of ground state molecules [1], present new experimental results for H₂ colliding with ionic surfaces and discuss the future of this new technique in terms of studying molecule-surface interaction-potentials and modifying the outcome of reactive molecule-surface collisions.

[1] Nature Communications, 8, 15357 (2017).

4:00pm SS+2D+AP+AS+OX+SE-ThA6 Diffusion of (100)-epitaxially Supported 3D fcc Nanoclusters: Complex Size-dependence on the Nanoscale, *King Chun Lai, J.W. Evans*, Iowa State University

Diffusion of supported 3D nanoclusters (NCs) followed by coalescence leads to coarsening of ensembles of supported NCs via Smoluchowski Ripening (SR) which is a key pathway for degradation of supported metal catalysts. The dependence of the NC diffusion coefficient, D_N, on size N (in atoms) is the key factor controlling SR kinetics, and traditional treatments assumed simple monotonic decrease with increasing size. We analyze a stochastic model for diffusion of (100)-epitaxially supported fcc NCs mediated by diffusion of atoms around the surface of the NC. Multiple barriers for surface diffusion across and between facets, along step edges, etc. are chosen to accurately describe Ag [Lai and Evans, Phys. Rev. Materials 3 (2019) 026001]. KMC simulations reveal a complex oscillatory variation of D_N with N. Local minima D_N sometimes but not always correspond to N = N_c where the equilibrium Winterbottom NC structure is a closed-shell. Local maximum generally correspond to N = N_c + 3. The oscillatory behavior is expected to disappear for larger N above O(10²). Behavior has similarities to but also basic differences from that for 2D supported NCs [Lai et al Phys. Rev. B 96 (2017) 235406]. Through detailed analysis of the energetics of the 3D NC diffusion pathway (which involves dissolving and reforming facets), we can elucidate the above behavior as well as observed trends in effective diffusion barrier.

4:20pm SS+2D+AP+AS+OX+SE-ThA7 Oxide Surface Formation on Rh Nanoparticle during O₂ Exposures Observed by Atom Probe Microscopy, *Sten Lambeets*, Pacific Northwest National Laboratory; *T. Visart de Bocarmé*, Université Libre de Bruxelles, Belgium; *N. Kruse*, Washington State University; *D.E. Perea*, Pacific Northwest National Laboratory

Metallic surfaces may undergo a series of surface and subsurface structural and chemical transformations while exposed to reactive gases that inevitably change the surface properties. Understanding such dynamics from a fundamental science point of view is an important requirement to build rational links between chemical/structural surface properties and design new catalysts with desired performance or new materials with enhanced resistance to corrosion. The research presented here addresses the early oxide formation dynamics on a rhodium (Rh) single nanoparticle during O₂ exposures and reveals the inter-facet cooperation between Rh{012} and Rh{113} facets, as well as the important role that the subsurface plays.

¹ Morton S. Traum Award Finalist

² National Student Award Finalist

³ National Student Award Finalist

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Field Ion and Field Emission Microscopies (FIM and FEM) enable correlative atomic to nanoscale imaging of the surface of a very sharp Rh needle, the apex size and shape of which models that of a Rh nanoparticle. FIM is used to map, with atomic lateral resolution, the Rh surface revealing a complex network of crystallographic facets, while FEM is used to observe and record O₂ dissociative adsorption and subsequent reaction with H₂ over this same surface of Rh in real-time with nano-scale lateral resolution. Since FEM imaging relies on local work function variations, it notably can be used to follow the fate of adsorbed oxygen atoms (O(ads)) on the Rh surface. As a result, we directly observe that the O₂ dissociative adsorption is mainly active on the Rh{012} regions. The application of Atom Probe Tomography (APT) provided a means to map the fate of the adsorbed oxygen leading to bulk oxide formation through Rh{113} facets. Thus the correlative combination of FIM, FEM, and APT provides unique insight into the mechanism of bulk oxide formation starting from the dissociative oxygen absorption occurring at {012} facets and subsurface penetration of the adsorbed oxygen occurring through {113} facets, leading to a preferential accumulation of the oxygen within the bulk along the [111] direction. This work offers a unique methodology to explore the interactions between the different crystal facets of a complex surface, to explore the complex dynamics linking the surface and the bulk, and finally, offers exciting perspectives leading to a better understanding of heterogeneous catalysis and corrosion dynamics.

4:40pm **SS+2D+AP+AS+OX+SE-ThA8 Noncontact AFM on Oxide Surfaces: Challenges and Opportunities**, *Martin Setvin*, TU Wien, Austria **INVITED**
Recent development of the noncontact atomic force microscopy (nc-AFM) has opened new possibilities in different fields – imaging of organic molecules [1], controlling the charge state of adsorbed species [2], or enhanced chemical resolution of surface atoms [3]. I will focus on the emerging possibilities and opportunities in the field of oxide surfaces and their surface chemistry.

The limits of atomic resolution will be illustrated on clean and water-exposed binary oxides like TiO₂, In₂O₃ or iron oxides. The enhanced chemical resolution of nc-AFM offers a unique opportunity for approaching complex materials with ternary chemical composition. This will be demonstrated on bulk-terminated perovskites SrTiO₃ and KTaO₃. A dedicated cleaving procedure [4,5] allows preparing flat regions terminated by domains of SrO/TiO₂ (or KO/TaO₂) with a well-defined atomic structure. The surface stability, point defects, electronic structure, and chemical properties of such surfaces will be discussed and linked to the incipient-ferroelectric character of these materials.

[1] Gross, L.; Mohn, F.; Moll, N.; Liljeroth, P.; Meyer, G., *Science* 2009, 325, 1110

[2] Gross, L.; Mohn, F.; Liljeroth, P.; Repp, J.; Giessibl, F. J.; Meyer, G., *Science* 2009, 324, 1428

[3] Sugimoto, Y.; Pou, P.; Abe, M.; Jelinek, P.; Perez, R.; Morita, S.; Custance, O., *Nature* 2007, 446, 64

[4] I. Sokolovic, M. Schmid, U. Diebold, M. Setvin, *Phys. Rev. Materials* 3, 034407 (2019)

[5] M. Setvin, M. Reticcioli, F. Poelzleitner, J. Hulva, M. Schmid, L. A. Boatner, C. Franchini, U. Diebold, *Science* 359, 572-575 (2018)

5:20pm **SS+2D+AP+AS+OX+SE-ThA10 Edge-Enhanced Oxygen Evolution Reactivity at Au-Supported, Ultrathin Fe₂O₃ Electrocatalysts**, *Xingyi Deng, D. Kauffman, D.C. Sorescu*, National Energy Technology Laboratory
Transition metal oxides have been emerging as promising candidates to replace the state-of-the-art IrO₂ electrocatalysts for oxygen evolution reaction (OER) in alkaline electrolyte, but their key structure-property relationships are often shadowed by heterogeneities in the typical catalyst samples. To circumvent this challenge, we have combined ultrahigh vacuum surface science techniques, electrochemical measurements, and density functional theory (DFT) to study the structure-dependent activity of well-defined OER electrocatalysts. We present direct evidence that the population of hydroxylated Fe edge-site atoms correlates with the OER activity of ultrathin Fe₂O₃ nanostructures (~0.5 nm apparent height) grown on Au(111) substrates, and the Fe₂O₃/Au catalysts with a high density of edge sites can outperform an ultrathin IrO_x/Au OER catalyst at moderate overpotentials. DFT calculations support the experimental results, showing more favorable OER at the edge sites along the Fe₂O₃/Au interface with lower predicted overpotentials resulted from beneficial modification of intermediate binding. Our study demonstrates how the combination of surface science, electrochemistry, and computational modeling can be

used to identify key structure-property relationships in a well-defined electrocatalytic system .

Bold page numbers indicate presenter

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 Acosta, A.: TF+EM+MI+MN+OX+PS-MoM3, 1
 Adamsen, K.C.: OX+EM+HC+MI+NS+SS+TF-TuA10, 5
 Alexandrowicz, G.: SS+2D+AP+AS+OX+SE-ThA3, **14**
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 Andersen, T.K.: OX+EM+MI+SS-WeM2, 8
 Ando, T.: OX+EM+HC+MI+NS+SS+TF-TuA3, 5
 Anwar, F.: OX+EM+MI+SS-WeM12, 9
 Armstrong, A.M.: EM+OX+TF-TuA12, 4
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 Balke, N.: TF+EM+MI+MN+OX+PS-MoM10, 2
 Bang, L.: HC+OX+SS-WeA2, 10
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 Biyikli, N.: EM+OX+TF-TuA8, **3**
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 Brann, M.R.: SS+2D+AP+AS+OX+SE-ThA1, **14**
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 Cunniff, A.: OX+EM+HC+MI+NS+SS+TF-TuA12, 6
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 Du, Y.: OX+EM+HC+MI+NS+SS+TF-TuA7, **5**; OX+EM+MI+SS-WeM1, 8

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 Hong, H.: OX+EM+MI+SS-WeM2, 8
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 Karim, R.: EM+OX+TF-TuA7, 3
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 Krok, F.: SS+AS+HC+OX-WeA12, 12
 Kruse, N.: SS+2D+AP+AS+OX+SE-ThA7, 14

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 Lee, H.: OX-TuP1, **7**
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 Lyle, L.A.M.: EM+OX+TF-TuA11, 4
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 Maria, J.-P.: OX+EM+MI+SS-WeM11, 9; TF+EM+MI+MN+OX+PS-MoM4, 1
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