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, Jeffry Kelber, University of North Texas

2:20pm OX+EM+HC+MI+NS+SS+TF-TuA-1 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-TuA-3 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.

4:20pm OX+EM+HC+MI+NS+SS+TF-TuA-7 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 bi-functional electrocatalyst, as an example, I will show how isovalent substitution, alliovalent 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.

5:00pm OX+EM+HC+MI+NS+SS+TF-TuA-9 Manipulate the Electronic Structures of Complex (Ni, Co) Oxides by Hole Doping for Oxygen Evolution Reaction, *Kelvin Zhang*, Xiamen University, China

This talk reports a fundmanetal study on the correlation of the composition and electronic structures of complex oxides with their electrocatalytic activity for oxygen evolution reaction (OER). In particular, we modulated the electronic states of complex oxides using hole doping strategy, e.g., Li doped NiO, Sr doped $LaFeO_3$ and Ni doped Co_3O_4. Photoemission spectroscopy and x-ray absorption spectroscopy (XAS) were used to study both the occupied and unoccupied density of states around the Fermi level. The electronic structures determines the adsorption strength of reaction intermediates for OER. Our results reveal two important change in the electronic structures induced by hole doping are crucial for improving OER activity: (1) upshift of the occupied valence band center to enhance the surface absorption; (2) creation of a new hole (unoccupied) state just above the Fermi level to reduces the energy barrier for electron transfer. Our results supplemented with DFT calculations established a direct correlation between the enhancement of activity with electronic structure, providing guideline for design of highly active electrocatalysts.

5:20pm OX+EM+HC+MI+NS+SS+TF-TuA-10 Vanadia/Tungsten Oxide on Anatase TiO2(101): a Model Catalyst Study by STM and XPS, *Tao Xu*, J Lauritsen, K 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 a-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 a- 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 a-TiO2 surface.

5:40pm **OX+EM+HC+MI+NS+SS+TF-TuA-11 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 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-TuA-12** *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.

Author Index

Bold page numbers indicate presenter

— A —
Adamsen, K: OX+EM+HC+MI+NS+SS+TF-TuA-10, 1
Ando, T: OX+EM+HC+MI+NS+SS+TF-TuA-3, 1
— B —
Binek, C: OX+EM+HC+MI+NS+SS+TF-TuA-1, 1
— C —
Cunniff, A: OX+EM+HC+MI+NS+SS+TF-TuA-12, 2
— D —
Dowben, P: OX+EM+HC+MI+NS+SS+TF-TuA-1, **1**
Du, Y: OX+EM+HC+MI+NS+SS+TF-TuA-7, **1**
— E —
Engelmann, S: OX+EM+HC+MI+NS+SS+TF-TuA-3, **1**

— H —
Huhtinen, H: OX+EM+HC+MI+NS+SS+TF-TuA-11, 2
— L —
Lauritsen, J: OX+EM+HC+MI+NS+SS+TF-TuA-10, 1
Liu, Y: OX+EM+HC+MI+NS+SS+TF-TuA-12, 2
— N —
Narayanan, V: OX+EM+HC+MI+NS+SS+TF-TuA-3, 1
— O —
Orvis, T: OX+EM+HC+MI+NS+SS+TF-TuA-12, **2**
— P —
Palai, R: OX+EM+HC+MI+NS+SS+TF-TuA-11, **2**

— R —
Ravichandran, J: OX+EM+HC+MI+NS+SS+TF-TuA-12, 2
— S —
Surendran, M: OX+EM+HC+MI+NS+SS+TF-TuA-12, 2
— W —
Wendt, S: OX+EM+HC+MI+NS+SS+TF-TuA-10, 1
— X —
Xu, T: OX+EM+HC+MI+NS+SS+TF-TuA-10, **1**
Xu, X: OX+EM+HC+MI+NS+SS+TF-TuA-1, 1
— Z —
Zhang, K: OX+EM+HC+MI+NS+SS+TF-TuA-9, **1**