

Wednesday Morning, October 31, 2012

Surface Science

Room: 22 - Session SS+OX-WeM

Synthesis and Characterization of Oxides

Moderator: J.M. Millunchick, University of Michigan

8:00am SS+OX-WeM1 Structure and Dynamics of Oxide Surfaces and Interfaces, X. Pan, University of Michigan INVITED

Ferroelectric materials are characterized by a spontaneous electric polarization that can be reoriented between different orientations by an applied electric field. The ability to form and manipulate domains with different polarization orientations at the nanometer scale is key to the utility of ferroelectric materials for devices such as nonvolatile memories. The ferroelectric switching occurs through the nucleation and growth of favorably oriented domains and is strongly mediated by defects and interfaces. Thus, it is critical to understand how the ferroelectric domain forms, grows, and interacts with defects. In this talk I will present the nanoscale ferroelectric switching of BiFeO_3 and $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ thin films under an applied electric field using *in situ* transmission electron microscopy with atomic resolution. We follow the kinetics and dynamics of ferroelectric switching at millisecond temporal and subangstrom spatial resolution. We observed localized nucleation events at the electrode interface, domain wall pinning on point defects, the formation of ferroelectric domains localized to the ferroelectric/electrode interface, and domain wall pinning by dislocations. We also find that in writing nanosized domains the domain wall itself can drive backswitching. It was observed that the localized 180° polarization switching in $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ thin films initially forms domain walls along unstable planes. After removal of the external field, they tend to relax to low energy orientations. In sufficiently small domains this process results in complete backswitching. Our results suggest that even thermodynamically favored domain orientations are still subject to retention loss, which must be mitigated by overcoming a critical domain size.

8:40am SS+OX-WeM3 Capturing Ion-Solid Interactions with MOS Structures, R. Shyam, E.S. Srinadhu, S. Chambers, J.E. Harriss, W.R. Harrell, C.E. Sosolik, Clemson University

We have fabricated metal-oxide-semiconductor (MOS) devices for a study of implantation rates and damage resulting from low energy ion-solid impacts. Specifically, we seek to capture ion irradiation effects on oxides by exposing as-grown SiO_2 layers (50 nm to 200 nm) to incident beams of singly-charged alkali ions with energies in the range of 100 eV to 5 keV. The oxide is analyzed post exposure by encapsulating the irradiated region under a top metallic contact or within a finished MOS device. Characterization of the resulting ion-modified MOS device involves the standard techniques of room temperature and bias-temperature stress capacitance-voltage (C-V) measurements. The C-V results reveal alkali ion-induced changes in the flatband voltage and slope of C-V of irradiated devices which can be used to extract and delineate between implantation probabilities and irradiation effects of the ions. Biased C-V measurements are utilized to confirm the concentration or dosage of ions in the oxide. A triangular voltage sweep (TVS) measurement at elevated temperatures also reveals the total ionic space charge in the oxide and is used to extract mobility for the ions as they pass through the damaged oxide. Our C-V data show changes in flatband voltage which are greater than those expected for mobile charges present at the range calculated by SRIM which implies that stoichiometry, morphological and chemical changes in the SiO_2 layer are introduced by the ion impacts.

9:00am SS+OX-WeM4 Synthesis and Characterization of Yttrium Aluminum Garnet and Lanthanum Zirconate Particles, R.R. Harl*, S.L. Gollub, G. Walker, B.R. Rogers, Vanderbilt University

Rare-earth doped yttrium aluminum garnet (YAG) and lanthanum zirconate (LZO) are luminescent ceramics that have been used in TV's, LED's, metal oxide transistors, and as laser sources. These materials are thermally and chemically stable. Recent work at Vanderbilt by the Walker and Rogers research groups has shown that the emitted spectrum of proton irradiated LZO particles differs from that of non-irradiated particles, suggesting these materials may be used as passive radiation exposure indicators.

We will discuss the combustion synthesis and characterization of YAG and LZO particles. Combustion synthesis involves heating a mixture of metal nitrates and a fuel until the mixture ignites. If the proper conditions are

used, the energy released by the combustion is sufficient to form polycrystalline material. The type and amount of fuel used in the synthesis affect the amount of gaseous by-products produced and flame temperature achieved during a reaction, both of which affect the crystallite size formed. The organic fuels included in this study are urea and glycine with adiabatic flame temperatures 1780°C and 1210°C, respectively. Urea's higher flame temperature makes this fuel attractive for combustion syntheses. However, urea shows signs of degradation beginning around 120 °C, well below its ignition temperature. Glycine does not appear to degrade until approximately 230°C much closer to its ignition temperature. The trade-off between degradation and adiabatic flame temperature suggests the temperature ramp rate used will significantly affect the performance of combustion syntheses carried out with these fuels.

We will present results of detailed thermogravimetric analysis and differential scanning calorimetry (TGA/DSC) experiments used to study the effects of heating rate on the combustion process and on the characteristics of the material formed. TGA/DSC-determined heats of combustion and heat capacities of the reactants and products will also be presented.

Characterization results of powders made using conditions determined by the TGA/DSC experiments will also be presented. X-ray photoelectron spectroscopy (XPS) was used to determine chemical bonding information. Rutherford backscattering spectroscopy (RBS) was used to provide quantitative elemental composition of the material. X-ray diffraction (XRD) was used to determine the crystallinity of the material and to estimate crystallite sizes. Photoluminescence spectroscopy (PL) was used to characterize the materials' emission spectra.

9:20am SS+OX-WeM5 X-ray Linear Dichroism of Epitaxial (Fe,N) Co-Doped Rutile TiO_2 Thin Films, T.C. Kaspar, Pacific Northwest National Lab, A. Ney, Univ. of Duisburg-Essen, Germany, A.N. Mangham, Pacific Northwest National Lab, S.M. Heald, Advanced Photon Source, Argonne National Lab, Y. Joly, Institut Néel, CNRS et Univ. Joseph Fourier, France, V. Ney, Univ. of Duisburg-Essen, Germany, F. Wilhelm, A. Rogalev, F. Yakou, European Synchrotron Radiation Facility, S.A. Chambers, Pacific Northwest National Lab

Efficient visible light photocatalysis could revolutionize hydrogen production, chemical synthesis, and pollution mitigation. Binary oxides such as TiO_2 have received much attention for these applications since they are stable under aqueous and oxidizing conditions, and show promise as ultraviolet-light photocatalysts. However, to operate in the visible portion of the solar spectrum, the wide bandgap of these oxides (~3 eV for rutile TiO_2) must be reduced. Anion doping of anatase TiO_2 has been widely explored, and shows some promise. However, in nanoparticles and fine powders, it can be difficult to determine the structural and electronic behavior of N dopants. Homoepitaxial $\text{Fe}:\text{TiO}_2$ and $(\text{Fe},\text{N}):\text{TiO}_2$ thin films deposited on rutile $\text{TiO}_2(110)$ were investigated by x-ray absorption spectroscopy (XAS) and associated theoretical simulations to elucidate the detailed structure of the doped materials. Co-doping with N was found to increase the extent of Fe incorporation into the rutile lattice. X-ray absorption near edge spectroscopy (XANES) spectra were collected at the Ti L-edge, Fe L-edge, O K-edge, N K-edge, and Ti K-edge. No evidence of structural disorder associated with a high concentration of oxygen vacancies was observed. Substitution of Fe for Ti could not be confirmed, although secondary phases such as Fe_2O_3 and metallic Fe could be ruled out. The similarity of the N K-edge spectra to O, and the presence of a strong x-ray linear dichroism (XLD) signal for the N K-edge, indicates that N is substitutional for O in the rutile lattice, and is not present as a secondary phase such as TiN. Simulations of the XANES spectra qualitatively confirm substitution, although N appears to be present in more than one local environment. Although optical absorption spectra confirm that substitutional N redshifts optical bandgap of Fe-doped rutile into the visible region, the film surfaces are photochemically inert with respect to hole-mediated decomposition of adsorbed trimethyl acetate.

9:40am SS+OX-WeM6 Unified Picture of the Excess Electron Distribution at the $\text{TiO}_2(110)$ Surface, P. Krueger, Institut Carnot de Bourgogne, France, J. Jupille, Institut des Nanosciences de Paris, France, S. Bourgeois, B. Domenichini, Institut Carnot de Bourgogne, France, A. Verdini, L. Floreano, A. Morgante, Laboratorio TASC, Italy

Titanium dioxide, an inert insulator in stoichiometric form, can be easily reduced into an n-type semiconductor TiO_{2-x} with the many electronic, photocatalytic and chemical properties that make the material of huge technological relevance. Formally associated with $\text{Ti}^{4+} + e^- \rightarrow \text{Ti}^{3+}$, the reduction of titania results in excess electrons (EE) that populate localized Ti 3d band gap states. Puzzling issues are the surface or subsurface distribution of EE and the lattice or interstitial nature (Ti_{im}) of the Ti^{3+} ions. Despite a number of experimental and theoretical studies, the reduced

* Morton S. Traum Award Finalist

archetypal TiO₂(110) has not been unambiguously pictured yet. Regarding the location of Ti³⁺ ions, density functional theory (DFT), DFT + U scheme and DFT-Hartree-Fock hybrid functionals (the two latter including a better account of self interaction corrections) are far from consensus. EE that are suggested to be trapped either on sixfold (Ti1) and fivefold (Ti2) coordinated surface Ti, or on subsurface beneath Ti1 or beneath Ti2. In such context, the unique capability of resonant photoelectron diffraction (RPED) to map out the spatial distribution of Ti 3d gap states was previously demonstrated in the study of a TiO₂(110) surface involving vacancies in bridging oxygen rows (O_b-vac) [1]. However, our conclusion that EE mostly occupy subsurface Ti sites was later challenged by the suggestion that Ti_{int} atoms play a key role in the formation of EE [2,3]. This has prompted us to analyse the Na-covered TiO₂(110) surface on which Na adatoms are predicted to produce similar EE as by direct injection of electrons [4], while the formation of Ti_{int} is not expected.

The pivotal observation was that the Na/TiO₂ RPED pattern [4] was almost perfectly similar to the O_b-vac RPED pattern [1]. Data were fitted on the basis of the location of the Ti³⁺ ions on the Ti lattice sites. Indeed, attempts to model EE on Ti_{int} failed. A unified model of the reduced TiO₂(110) surface emerges, with EE located on subsurface beneath Ti2 > second subsurface beneath Ti1 > Ti1 [4] (See supplemental document). As shown by the qualitative agreement of the present findings with DFT approaches [5,6], the charge distribution of the Ti 3d states is dictated by electrostatics. It is essentially an intrinsic property of the titania surface that is independent on the way EE are created.

- [1] Krueger et al. Phys. Rev. Lett. 100 (2008) 055501.
- [2] Wendt et al., Science 320 (2008) 1755.
- [3] Papageorgiou et al., Proc. Natl. Acad. Sci. U.S.A. 107 (2010) 2391.
- [4] Krueger et al. Phys. Rev. Lett. 108 (2012) 126803.
- [5] Albaret et al., Phys. Rev. B 65 (2001) 035402.
- [6] Deskins et al., J. Phys. Chem. C 113 (2009) 14583.

10:40am **SS+OX-WeM9 XPS Satellite Structure and Covalent Bonding**, *P.S. Bagus*, University of North Texas, *E.S. Ilton*, Pacific Northwest National Laboratory, *C.J. Nelin*, Consultant

The satellites in X-Ray photoemission spectroscopy, XPS, especially for ionic compounds, are an important part of the spectra [1, 2] and may provide information about the electronic structure. For uranium oxides, they allow the oxidation state of the U cations to be determined. [2] It would be useful to establish and to understand how the satellite intensity may be related to the extent of covalent bonding in an oxide or other ionic material. It is often believed that the intensity lost from the main XPS peaks to satellites is directly related to the covalent bonding, with greater covalent bonding leading to greater losses to satellites. We show that this relationship is not rigorously correct. A more correct relationship is between satellite intensity and the difference of the degrees of covalency in the initial, unionized, state and the final, core-hole states with larger differences leading to larger losses to satellites. Furthermore, the final state covalency is less sensitive to the environment than is the initial state covalency since the bonding in the final state is more appropriate to that for an equivalent, Z+1, impurity atom representing the core-ionized atom. [3] We investigate the extent to which the effects of covalency can be tuned by comparing the Ni 2p XPS between NiO and Ni impurities in MgO.

1. P. S. Bagus, et al., Chem. Phys. Lett. **487**, 237 (2010).
2. E. S. Ilton and P. S. Bagus, Surf. Interface Anal. **43**, 1549 (2011).
3. W. L. Jolly and D. N. Hendrickson, J. Am. Chem. Soc. **92**, 1863 (1970).

11:00am **SS+OX-WeM10 Surface of BaTiO₃ (001): STM and STS Study**, *E. Morales*, *J. Martinez*, *A.M. Rappe*, *D.A. Bonnell*, University of Pennsylvania

BaTiO₃ is a versatile material that finds applications in sensors and electrooptical devices. Interactions start at the very surface, thus it is necessary to understand at a fundamental level its geometrical and electronic structure. Ferroelectricity is a key property that provides unique opportunities to explore molecular adsorption at a surface and allows investigation of chemical interactions as well. Interaction with gaseous species can be performed in-situ in "as-received" and poled crystals by controlling the poling voltage at the surface. Recent studies with macroscopic measurements show that polarization indeed affects molecular adsorption but mechanisms are not yet understood. Here we present scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) of atomically resolved reconstructions on BaTiO₃ (001) surfaces, (√5x√5)R26.6^o. A comparison of electronic structure determined by STS with theoretical calculations shows that the surface that is Ti terminated. In this and other reconstructions Ti-ad atoms create filled and empty states that are imaged in STM. The interactions of reconstructed

surfaces with H₂O is examined with atomic resolution. This is the first atomic scale observation of molecular adsorption on a ferroelectric surface.

11:20am **SS+OX-WeM11 Synthesis and Characterization of White Light Emitting Ca_xSr_{1-x}Al₂O₄:Tb³⁺,Eu³⁺ Phosphor**, *S.K. Shaat*, *H.C. Swart*, *O.M. Ntwaeaborwa*, University of the Free State, South Africa

Today, many researchers are making efforts to develop white light emitting phosphors that can be used in solid state lighting applications such as phosphor lamps and light emitting diodes. Aluminates with a general formula MAl₂O₄ (M = Ba, Ca, Mg, Sr) have emerged as preferred hosts for divalent (Mn²⁺ and Eu²⁺) and trivalent (Ce³⁺, Tb³⁺, Dy³⁺) ions to prepare such phosphors. We have prepared a potential white light emitting Ca_xSr_{1-x}Al₂O₄:Tb³⁺,Eu³⁺ (x = 0, 0.3, 0.7, 1) phosphor by combustion method and we are evaluating it for application in solid state lighting. Depending on the concentration of Ca²⁺ or Sr²⁺, the X-ray diffraction data showed that monoclinic structures of either CaAl₂O₄ or SrAl₂O₄ were crystallized and the stretching modes of Sr-Al-O and Ca-Al-O bonds were confirmed from the Fourier transform infrared spectroscopy data. The chemical compositions and electronic states of each elements of the Ca_xSr_{1-x}Al₂O₄:Tb³⁺,Eu³⁺ phosphor were determined using X-ray photoelectron spectroscopy. White photoluminescent was observed when Ca_xSr_{1-x}Al₂O₄:Tb³⁺,Eu³⁺ was excited at 227 nm using a monochromatized xenon lamp. This was a result of the combination of blue and green emissions from Tb³⁺ and red emission from Eu³⁺. It is likely that Tb³⁺ and Eu³⁺ ions were simultaneously excited by a single photon of sufficiently high energy absorbed in Ca_xSr_{1-x}Al₂O₄ host.

11:40am **SS+OX-WeM12 A Novel 2-D Cu-Tungstate (CuWO_x) Phase on Cu(110)**, *F.P. Netzer*, *M. Denk*, *D. Kuhnness*, *M. Wagner*, *S. Surnev*, University of Graz, Austria, *F.R. Negreiros*, *L. Sementa*, *G. Barcaro*, *A. Fortunelli*, CNR-IPCF Pisa, Italy

We explore the feasibility to fabricate W-oxide nanostructures on metal surfaces via self-assembly and condensation of (WO₃)₃ clusters, deposited directly from the gas phase: here we report the formation of a novel two-dimensional Cu-tungstate CuWO_x phase on Cu(110). A beam of (WO₃)₃ cluster molecules, formed by sublimation of WO₃ powder at ~900-1000°C in a thermal evaporator, has been directed onto a Cu(110)2x1-O surface oxide at low temperature and the surface has been annealed subsequently at 600 K. At low temperature (< 15 K) the (WO₃)₃ clusters adsorb in intact molecular form, albeit in a somewhat distorted cluster geometry [1]. Upon heating to 600K, the (WO₃)₃ molecules dissociate and react with the Cu-O(2x1) surface oxide, forming a wetting monolayer with a well ordered incommensurate structure. The latter has been structurally characterized by high-resolution STM imaging and LEED. The chemical nature and electronic structure of this novel 2-D W-O-Cu layer has been investigated by high-resolution XPS core level spectroscopy, NEXAFS, and valence band spectra. The unusually sharp W 4f core level spectra, the specific NEXAFS fingerprint and the evolution of the valence band all suggest that this 2-D W surface oxide is of a Cu-tungstate CuWO_x type. Density functional calculations are in progress to help elucidating the physical and chemical nature of this unusual surface oxide phase.

Work supported by the ERC Advanced Grant SEPON

- [1] M. Wagner, S. Surnev, M.G. Ramsey, G. Barcaro, L. Sementa, F.R. Negreiros, A. Fortunelli, Z. Dohnalek, F.P. Netzer, J. Phys. Chem. C **115** (2011) 23480

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