Tuesday Morning, November 11, 2014

Surface Science
Room: 309 - Session SS+AS+EN-TuM

Synthesis, Structure and Characterization of Oxides
Moderator: Andrew Gellman, Carnegie Mellon University

8:00am **SS+AS+EN-TuM1 Coexisting Accessible Surface Phases on $BaTiO_3$ (001)**, ***Erie Morales***, *J.M. Martirez,* University of Pennsylvania, *W.A. Saidi,* University of Pittsburgh, *A.M. Rappe, D.A. Bonnell,* University of Pennsylvania

Novel ferroelectric $BaTiO_3$ applications ranging from sensors to nanogerators require a detailed understanding of atomic interactions at surfaces. Single crystals provides a platform that allows the explotation of surface physical and chemical properties that can be readily transferred to other ABO_3 perovskite structures. The processes that result in the atomic and electronic structures of surfaces in tandem with details of surface reactivity are necessary steps towards an understanding of $BaTiO_3$. Here we demonstrate that two surface reconstruction phases can coexist on a surface and explain the stability of the surface with a quantitative comparison of thermodynamic and kinetic considerations. Specifically, scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) of atomically resolved c(2x2) and c(4x4) reconstructions on $BaTiO_3$ (100) are compared with density functional theory models to determine the structures of the phases. First principles calculations are also used to examine the thermodynamic stability of the phases and the reaction pathways to both the stable and meta stable structures. We also show the atomic structures of 1 D interfaces between the phases. The ferroelectric properties of $BaTiO_3$ lead to polarization dependent surface reactions and recent results based on poling at atomic level and will be discussed.

8:20am **SS+AS+EN-TuM2 Oxidation and Chemical Reactivity of TbO_x Thin Films on Pt(111)**, *W. Cartas, R. Rai, A. Sathe,* University of Florida, *A. Schaefer,* University of Bremen, Germany, ***Jason Weaver***, University of Florida

Rare earth oxides (REOs) exhibit favorable catalytic performance for a diverse set of chemical transformations, including both partial and complete oxidation reactions. In this talk, I will discuss our recent investigations of the growth, oxidation and chemical reactivity of TbO_x(111) thin films on Pt(111), and make comparisons with results for Sm_2O_3(111) films grown on the same substrate. Bulk terbia and samaria represent examples of REOs that are reducible vs. effectively irreducible, respectively. From low energy electron diffraction and scanning tunneling microscopy, we find that samaria and terbia grow as high quality thin films on Pt(111) during deposition in ultrahigh vacuum. Both oxides develop in the Ln_2O_3 stoichiometry and adopt an oxygen-deficient fluorite structure wherein the metal cations form a hexagonal lattice in registry with the Pt(111) substrate, while oxygen vacancies are randomly distributed within the films. We find that plasma-generated O-atom beams are highly effective in transforming the Tb_2O_3(111) films to higher Tb oxides. Based on results of X-ray photoelectron spectroscopy and O_2 temperature programmed desorption (TPD), we show that exposure to O-atom beams completely oxidizes the Tb_2O_3(111) films to TbO_2 at 300 K, for film thicknesses up to at least seven layers. Heating to ~1000 K in UHV restores the films to the Tb_2O_3(111) stoichiometry, and produces O_2 desorption in two distinct TPD features centered at ~370 K and 660 K which we attribute to oxygen release from lattice sites located in the surface vs. bulk layers, respectively. We also find that O-atom adsorption at 90 K produces a weakly-bound state of oxygen on the TbO_x films which desorbs between ~100 and 270 K. This state of oxygen may correspond to a form of chemisorbed oxygen on the TbO_x film. Consistent with this interpretation, TPD experiments performed after oxidizing a $Tb_2{}^{18}O_3$ film with ^{16}O-atoms demonstrate that oxygen desorption below about 500 K originates only from the oxygen that is “added” to the Tb_2O_3 film, while all isotopic combinations of O_2 desorb from the bulk above 500 K. Lastly, I will present results which show that the oxidized TbO_x films exhibit high activity and selectivity for the dehydrogenation of methanol to formaldehyde, whereas the initial Tb_2O_3 films have limited reactivity toward methanol.

8:40am **SS+AS+EN-TuM3 Structure/Function Relationships on Cerium Oxide: Reactions on Single Crystal Films and Shape-Selected Nanocrystals**, ***David Mullins***, Oak Ridge National Laboratory **INVITED**

Cerium oxide is a principal component in many heterogeneous catalytic processes. One of its key characteristics is the ability to provide or remove oxygen in chemical reactions. Recent work has demonstrated how the reactivity and selectivity of various molecules are dramatically altered on different crystallographic faces of cerium oxide. The structure and composition of different faces determine the number of coordination vacancies (CV) surrounding surface atoms, the availability of adsorption sites, the spacing between adsorption sites and the ability to remove O from the surface. The Ce cation sites are less accessible and have fewer coordination vacancies (CV) on CeO_2(111) than on CeO_2(100). Even though the Ce is in the second layer on CeO_2(100), molecules can adsorb in the open bridge sites between two Ce cations. While there have been numerous studies of the adsorption and reaction of various molecules on CeO_2(111) only recently have comparable experiments been conducted on CeO_2(100).

To investigate the role of surface orientation on reactivity, CeO_2 films with different orientations were grown by two different methods. CeO_2(100) films were grown ex situ by pulsed laser deposition on Nb-doped $SrTiO_3$(100). CeO_2(111) films were grown in situ by thermal deposition of Ce metal onto Ru(0001) in an oxygen atmosphere. The chemical reactivity was characterized by the adsorption and decomposition of various molecules such as CO_2, H_2O, alcohols, aldehydes and organic acids. In general the CeO_2(100) surface was found to be more active, i.e. molecules adsorbed more readily and reacted to form new products, especially on a fully oxidized substrate. However the CeO_2(100) surface was less selective with a greater propensity to produce CO, CO_2 and water as products. Experiments are underway to determine if CeO_2(110), where the Ce adsorption sites are in the top layer and have 2 CV but the O has only 1 CV, will produce an active yet more selective catalyst.

It is possible to synthesize high surface area shape-selected nanoparticles (octahedra and cubes), i.e. powders that expose a single, well-defined surface. Experiments have shown similarities between the single crystal surfaces and shape-selected nanoparticles, e.g. CeO_2(111)/octahedra are less active than CeO_2(100)/cubes. However there have also been significant differences in selectivity and the types of products formed. Possible explanations for the differences on the single crystal surfaces vs. the nanoshapes will be considered.

Research sponsored by the US Department of Energy, Office of Science, Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division.

9:20am **SS+AS+EN-TuM5 Ceria on Cu(110): Formation of Nanostripe Strain Defects**, *L. Ma, N. Doudin, S. Surnev,* ***Falko Netzer***, Karl-Franzens University, Austria

The growth morphology and atomic geometry of ceria nanostructures on Cu(110) have been investigated by STM, LEED and XPS. Ceria grows epitaxially in a two-dimensional (2-D) hexagonal layer, which is associated with a CeO_2(111)-type trilayer structure forming a (3x11) coincidence lattice. An important experimental parameter is the oxygen pressure during growth: it influences the stoichiometry of the ceria overlayer as well as the Cu surface oxide phase, which coexists with the ceria for coverages below the full monolayer. For oxygen pressures in excess of 10^{-7} mbar, stoichiometric CeO_2 and coexisting Cu-c(6x2) surface oxide are formed, whereas for lower oxygen pressures, in the 10^{-8} mbar range, slightly substoichiometric ceria ($CeO_{\sim 1.9}$) and a Cu-(2x1) surface oxide are observed. The ceria overlayer grows essentially 2-D, but displays a peculiar nanostripe pattern, with varying periodicities ranging from 4-8 nm and a corrugation amplitude of 0.2-0.3 nm. This nanostripe pattern is due to a topographic modulation of the overlayer caused by the frustration of overlayer-substrate bonding as a result of the epitaxial mismatch at the ceria-Cu interface. Detailed STM investigation reveals a distortion of the ceria lattice in the transition region between dark (low) and bright (high) stripes, which gives rise to periodic regions of anisotropic lattice strain - socalled "lattice strain defects". It is speculated that these lattice strain defects may support particular chemical reactivity.

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9:40am **SS+AS+EN-TuM6 Design Rules for Stabilizing Polar Metal Oxide Surfaces: Adsorption of O_2 on Zn-rich Polar ZnO(0001)**, ***Ming Li***, *P. Gorai, E. Ertekin, E.G. Seebauer,* University of Illinois at Urbana-Champaign

For oxide semiconductors with appreciable ionic character, under-coordination of the surface atoms leads to thermodynamic instability that is typically restored by reconstruction, faceting, or extensive surface defect creation. Developing design rules for stabilizing polar metal oxide surfaces that avoid these phenomena could offer novel protocols for applications such as improved nanostructure growth and design of photocatalytic heterostructures. The present work describes calculations by density functional theory for Zn-rich polar ZnO(0001) which demonstrate that stabilization via chemisorbed O_2 together with vacancy formation is energetically as favorable as stabilization by vacancies alone. The stabilization mechanism including adsorption is so effective that it promotes O_2 adsorption to an extent that is not possible on non-polar ZnO. Experimental evidence for such stabilization behavior is presented based on measurements of O_2 adsorption on polar ZnO(0001) via the optical modulation technique of photoreflectance. The measured isotherms yield a sizable adsorption enthalpy of adsorption near 1.8eV, confirming a strong interaction with the polar surface.

11:00am **SS+AS+EN-TuM10 The Growth of Catalytic Thin Films on a Polar Substrate: Cr_2O_3 on ZnO (0001) and ZnO (000-1)**, ***Xiaodong Zhu***, Yale University

Zinc oxide is a wurtzite-structured polar crystal with dramatic polarization direction-dependent surface chemistry. Meanwhile, chromium III oxide is a non-polar material catalytically active for a number of industrial chemical reactions, most notably dehydrogenation. Therefore, the Cr_2O_3/ZnO system has been chosen to demonstrate how the polarization direction of a substrate can be exploited tailor the surface properties of catalytically active non-polar thin films. Photoelectron spectroscopy and electron diffraction have been performed to determine the growth mode as well as the film quality. The growth is 2D; however, the films appear initially disordered on both positive and negatively poled substrates. On both substrates the order was observed to improve with thickness. Small band offsets between Cr_2O_3 and oppositely poled substrates were observed that were consistent with charge compensation at the Cr_2O_3/ZnO interface. No obvious change in the oxidation state of the chromium was seen and so it is assumed that the charge compensation at the interface only involves Zn and/or O. The offset between the Cr peaks on positively and negatively poled substrates was obvious at the initial growth stages but then decayed with film thickness, suggesting that the compensating charges at the interface may migrate to the film surface. Valence band spectra were analyzed to characterize the bonding at the interface. The surface chemical behavior of Cr_2O_3 on the two zinc oxide surfaces is being characterized to determine how significantly the polar interface impacts the surface properties of thin supported layers.

11:40am **SS+AS+EN-TuM12 Chemical Characterization of Elements in Oxides using X-ray Satellite Lines**, ***Terrence Jach***, National Institute of Standards and Technology (NIST)

X-ray satellite lines come about in x-ray fluorescence spectroscopy as a result of shake-off events in the excitation process. The ratio of their intensities has been shown to be a sensitive function of their oxidation states. We are able to observe the K satellite lines in the x-ray spectra of oxides and glasses, excited by the beam of an electron microscope and detected by a high resolution x-ray microcalorimeter detector. The results show surprising departures from the expected states of some metal elements that we expect to be fully oxidized. The satellite ratio is a way of determining the chemical environment of insulators without charging or ultra-high vacuum.

12:00pm **SS+AS+EN-TuM13 *In Situ* XPS and NRA Studies of Hydrogen Diffusion in TiO_2 Single Crystals**, ***Vaithiyalingam Shutthanandan***, *M.I. Nandasiri, S.A. Thevuthasan, M.A. Henderson, S. Manandhar*, Pacific Northwest National Laboratory

The intrinsic point defects associated with oxygen vacancies and Ti^{3+} ions play a crucial role in the usage of titanium dioxide (TiO_2) in various technological applications including catalysis and photochemistry. It is well known that the interactions between H atoms and surface oxygen in TiO_2 lead to the formation of Ti^{3+} ions at elevated temperatures. However the Ti^{3+} ion formation and accumulation as a function of elevated temperatures in UHV conditions during hydrogen diffusion in TiO_2 is not well understood. In this study, we have used ion implantation method to incorporate hydrogen in single crystal TiO_2 (110) samples and investigated the behavior of point defects in both pure and hydrogen implanted TiO_2 as a function elevated temperatures using Rutherford backscattering spectrometry (RBS), nuclear reaction analysis (NRA), x-ray photoelectron spectroscopy (XPS) and ultra violet photoemission spectroscopy (UPS). TiO_2 single crystals were implanted with 40 keV hydrogen ions at room temperature with ion fluences of $1x10^{15}$, $1x10^{15}$ and $1x10^{17}$ atoms/cm^2. Samples were isochronally annealed in vacuum for 30 minutes at each temperature up to 1100K and hydrogen and Ti^{3+} defects were quantified. Hydrogen depth profile measurements obtained from $1x10^{17}$ atoms/cm^2 implanted sample reveal that hydrogen diffused towards the surface at lower temperatures and it slowly diffuses out from the samples at higher temperatures. XPS and UPS measurements from the hydrogen implanted samples show significantly higher Ti^{3+} defects in comparison to pure TiO_2 at these temperatures under UHV conditions. These defects reach a maximum around 880 K in which almost all hydrogen was removed from the sample. When the implanted sample further annealed to high temperatures, the amount of Ti^{3+} in hydrogen implanted samples started to decrease and reaches the values from the pure TiO_2 samples around 1100K.

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