Thursday Morning, October 18, 2007

Surface Science

Room: 608 - Session SS1-ThM

Oxide Surface Structure II

Moderator: F.P. Netzer, Karl-Franzens University Graz, Austria

8:00am SS1-ThM1 Observation of a ($\sqrt{3}$ x $\sqrt{3}$)R30° Reconstruction on ZnO (000-1), *S.T. King*, S.S. Parihar, K. Pradhan, H.T. Johnson-Steigelman, University of Wisconsin - Milwaukee, Z. Zhang, P. Zschack, Argonne National Laboratory, P.F. Lyman, University of Wisconsin - Milwaukee
High energy polar-terminated metal oxide surfaces stabilize by a fascinating set of energy-lowering mechanisms.[1] While MgO(111) and NiO(111) stabilize via a sequence of surface reconstructions, most studies have shown that the (0001) (Zn-polar) and (000-1) (O-polar) faces of ZnO remain unreconstructed. Surface stabilization has been attributed to incomplete charge transfer between the Zn- and O-polar surfaces resulting in metallic surface states.[2] However, a recent He-atom scattering study of H-free ZnO (000-1) observed a (1x3) reconstruction, which de-reconstructs upon H exposure.[3] We extend the knowledge of ZnO surface reconstructions by investigating a ($\sqrt{3}$x$\sqrt{3}$)R30° reconstruction on ZnO (000-1) by low energy electron diffraction, x-ray photoelectron spectroscopy, and surface x-ray diffraction. While this reconstruction has been observed on the (0001) face,[4] to our knowledge this is the first reported observation on the O-polar surface. The implications of this reconstruction on understanding ZnO surface stabilization mechanisms will be discussed.

[1] C. Noguera, J. Phys.: Condens. Matter 12, R367 (2000)
[2] A. Wander et al., Phys. Rev. Lett. 86, 3811 (2001)
[3] M. Kunat et al., Phys. Rev. B 66, 081402(R) (2002)
[4] Y. Margoninski and R. E. Kirby, J. Phys. C 8, 1516 (1975)

8:20am SS1-ThM2 $Cu_xNi_{1-x}O$ and $Zn_xNi_{1-x}O$ Rocksalt Oxide Surfaces: Novel Environment for Cu^{2+}, Zn^{2+} and Its Effect on the NiO Electronic Structure, K.J. Gaskell, *M.A. Langell*, University of Nebraska
The effect on surface composition, electronic structure and bonding has been investigated for rocksalt $Cu_xNi_{1-x}O$ and $Zn_xNi_{1-x}O$ solid solutions, which form at the nickel-rich end of the phase diagram up to approximately x = 0.3. Octahedral coordination presents an unusual environment in solid state oxides for the "guest" Cu^{2+} and Zn^{2+} cations, and their bonding properties can be shown to be significantly different in the rocksalt environment. For example, ab initio calculations of the $Zn_xNi_{1-x}O$ valence band structure indicate that zinc interacts with the lattice oxygen primarily through the Zn 4s orbitals and is less covalent than in wurtzite ZnO. Photoemission results also provide insight into the bonding, and the Ni 2p photoemission changes substantially with increased guest ion concentration due to attenuation in non-local screening effects. The charge-transfer nature of the NiO electronic structure, however, remains largely intact. Auger parameter analysis confirms that the guest ions are octahedrally coordinated, and Auger and x-ray photoelectron spectroscopies show comparable surface and bulk concentrations until phase separation occurs.

8:40am SS1-ThM3 Surface Study of In_2O_3 and Sn-doped In_2O_3 Thin Films with (100) and (111) Orientations, *E.H. Morales*, Tulane University, M. Batzill, University of South Florida, U. Diebold, Tulane University
In_2O_3 and Sn-doped In_2O_3 (Indium-Tin Oxide, ITO) exhibit optical transparency combined with low electrical resistivity, and find application in flat panel displays and solar cells. Relatively little is known about their atomic-scale surface properties, mainly because of challenges in preparing single crystal samples. We have grown epitaxial In_2O_3 and ITO films on Yttrium Stabilized Zirconia. The (100) surface has polar character, and the (111) orientation is non-polar. The films were prepared using oxygen-plasma assisted electron beam epitaxy in ultra high vacuum (UHV) conditions. The growth was monitored with Reflection High Energy Electron Diffraction (RHEED). Samples were characterized with X-ray Photoemission Spectroscopy (XPS) and Angle Resolved XPS (ARXPS) using Al-Ka radiation and Low Energy Electron Diffraction (LEED) in-situ, as well as synchrotron-based Ultra-Violet Photoemission Spectroscopy (UPS) . The films were stoichiometric, except for ITO(100), where ARXPS indicates Sn segregation. In_2O_3 (100) shows faceting in LEED, while ITO(100) stays flat with a 1x1 surface termination. Thus, it appears that Sn-segregation to the surface stabilizes the polar In_2O_3 (100). In_2O_3 (111)

exhibits a ($\sqrt{3}$x$\sqrt{3}$)R30° reconstruction in LEED. Up to 9 at% Sn in ITO (111) does not seem to alter this reconstruction. Resonant photoemission measurements indicate a Sn-derived band gap state with resonance at 30 eV photon energy on the ITO (100) film; this gap state is far less pronounced on ITO (111). Interestingly, the valence band maximum is located at 2.5 and 2.7 eV below the (surface) Fermi level for ITO (100) and (111), respectively. This is ca. 1 eV higher than expected for a heavily n-type doped material with a direct optical band gap of 3.7 eV. Reasons for this apparent discrepancy will be discussed.

9:00am SS1-ThM4 Structure of the Polar Oxide Surface MgO(111) ($\sqrt{3}$ x $\sqrt{3}$)R30°, *S.E. Chamberlin*, H.C. Poon, D.K. Saldin, C.J. Hirschmugl, University of Wisconsin - Milwaukee
Structures of polar oxide surfaces have been of great interest with several models proposed to compensate the "polar surface instability problem," including 1.) adsorption of foreign species, e.g. a hydroxylated surface, 2.) surface faceting, and 3.) metallization.[1] MgO(111), the polar surface of a prototypical rocksalt structure, has been shown to maintain a 1x1 structure when annealed to low temperatures and reconstruct when heated to higher temperatures,[2] and thus represents an ideal system for detailed structural analysis. Detailed surface structure for the 1x1 and progress towards a structure for the ($\sqrt{3}$ x $\sqrt{3}$)R30° reconstruction will be presented. The data have recently been obtained with a novel, low-current delay-line-detector LEED (DLD-LEED) system to minimize electron damage. An hydroxylated 1x1 surface was found to be in good agreement with photoelectron diffraction and electronic structure calculations,[3] but LEED-IV and Direct Methods results for the MgO(111) ($\sqrt{3}$ x $\sqrt{3}$)R30° will be shown where the structure does not agree with previously published models.[2,4]

References
[1] C. Noguera, J. Phys.: Condens. Matter 12, R367 (2000)
[2] R. Plass, K. Egan, C. Collazo-Davila, D. Grozea, E. Landree, L.D. Marks, M. Gajdardziska-Josifovska, Phys. Rev. Lett. 81, 4891 (1998)
[3] V.K. Lazarov, R. Plass, H.C. Poon, D.K. Saldin, M. Weinert, S.A. Chambers, M. Gajdardziska-Josifovska, Phys. Rev. B 71, 115434 (2005)
[4] A. Subramanian, L.D. Marks, O. Warschkow, D.E. Ellis, Phys. Rev. Lett. 92, 200411 (2004)

9:20am SS1-ThM5 Monocrystalline TiO_2 Nanoparticles Growth on Au(111) Surface by RLAD Method, *D.V. Potapenko*, Columbia University, J. Hrbek, Brookhaven National Laboratory, R.M. Osgood, Columbia University
Titanium oxide is a promising photocatalytic material and has been the subject of much research throughout the last two decades. Nanostructuring is one approach for tailoring the properties of a catalyst. Recently, two methods of preparation of titania nanoparticles on Au(111) surfaces were reported (Z. Song at al. 2005 and E. Farfan-Arribas et al. 2005); yet no light-induced chemistry was observed on such nanoparticles to date. In order to prepare photoactive nanoparticles, we have conducted an extensive STM study of the growth of TiO_2 on a Au(111) surface by Reactive Layer Assisted Deposition (RLAD). The method consists of physical vapor deposition of Ti on a predeposited layer of oxygen-containing reactant followed by annealing to a higher temperature that removes the excess of the reactant. In the experiments with water as a reactive layer, we investigated the dependence of morphology of the produced arrays of titania nanoparticles on the thickness of the water multilayers. At water coverages above 50 ML we found evidence for role of an intermediate liquid water layer formed as the temperature is increased. The dynamics of water evaporation, rather than the underlying Au surface reconstruction, determined the particle distribution on the surface in this case. This relatively thick water layer also has caused us to observe evidence of the titanium hydride formation. At temperatures above 300 K the hydride decomposed leaving the titanium buried under a gold layer. The typical size of initially formed titania nanoparticles was 1 nm. At more elevated temperatures, nanoparticles coalesced so that by a temperature of 900 K about 80 % of the titania material was converted into single-crystal, flat islands with edges parallel to Au [1-10] directions, with their heights being a multiple of 0.55 nm. The atomic structure of the islands will be discussed. We have also attempted to use NH_4NO_3 as a reactive layer and the corresponding results will be presented.

9:40am SS1-ThM6 Reactive Ballistic Deposition of Porous TiO_2 Films, *D.W. Flaherty*, University of Texas at Austin, Z. Dohnálek, Pacific Northwest National Laboratory, T.E. Engstrom, University of Texas at Austin, A. Dohnálková, B.W. Arey, D.E. McCready, N. Ponnusamy, Pacific Northwest National Laboratory, C.B. Mullins, University of Texas at Austin, B.D. Kay, Pacific Northwest National Laboratory
Nanoporous, high-surface area films of TiO_2 are synthesized by reactive ballistic deposition of titanium metal in an oxygen ambient.[1] Auger electron spectroscopy (AES) is used to investigate the stoichiometric dependence of

the films on growth conditions (surface temperature and partial pressure of oxygen). Scanning and transmission electron microscopies show that the films consist of arrays of separated filaments. The surface area and the distribution of binding site energies of the films are measured as functions of growth temperature, deposition angle, and annealing conditions using temperature programmed desorption (TPD) of N_2. TiO_2 films deposited at 50 K at 70° from substrate normal display the greatest specific surface area of 100 m^2/g. In addition, the films retain greater than 70% of their original surface area after annealing to 600 K. The combination of high surface area and thermal stability suggests that these films could serve as supports for applications in heterogeneous catalysis. The research described in this presentation was performed in the Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by the Department of Energy's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory.

[1] David W. Flaherty, Zdenek Dohnálek, Alice Dohnálková, Bruce W. Arey, David E. McCready, Nachimuthu Ponnusamy, C. Buddie Mullins, and Bruce D. Kay, J. Phys. Chem. C 111 (2007) 4765-4773.

10:00am SS1-ThM7 Complexities and Surprises in the Epitaxial Growth of Pure and Doped TiO₂, *S.A. Chambers*, Pacific Northwest National Laboratory INVITED

TiO_2 is a transition metal oxide of considerable interest in several areas of surface, interface and thin-film science. Recent cation doping film growth studies show that certain transition metal dopants with unpaired d electrons, in concert with structural defects, impart a new form of high-temperature ferromagnetism in which dopant spins are aligned by electrons associated with the defects.[1-3] Anion (principally N) doping film growth studies show that substitutional N gives rise to a substantial red shift in the bandgap, paving the way for enhanced visible solar light absorption and the associated photophysical and photochemical energy conversion processes. However, N, which should be an acceptor in TiO_2, is actually fully compensated by conduction band electrons from interstitial Ti(III), which in turn results from Ti indiffusion during growth.[4,5] These insights were gained by our ability to grow and painstakingly characterize very well-defined, high-quality epitaxial films of pure and doped TiO_2. In the process of growing these materials with an unprecedented level of control, we have learned a great deal about the nucleation and growth of the different polymorphs of TiO_2.[6] The roles of atomic fluxes, growth temperature, dopants, overall growth rate and substrate structural properties have been elucidated one by one, and these results constitute a rich source of insight into the way transition metal oxide films nucleate and grow. In this talk, I will give an overview of our work on pure and doped rutile and anatase homoepitaxy and heteroepitaxy. This work has been supported by the US DOE, Office of Science, Division of Materials Science and Engineering, and Division of Chemical Sciences.

[1] T. C. Kaspar et al., Phys. Rev. Lett. 95, 217203 (2005).
[2] T. C. Kaspar et al., J. Vac. Sci. & Technol. B 24, 2012 (2006).
[3] T. C. Kaspar et al. Phys. Rev. B 73, 155327 (2006).
[4] S. H. Cheung et al., Surf. Sci. 601, 1754 (2007).
[5] S. A. Chambers et al., Chem. Phys., to appear (2007).
[6] R. Shao et al., Surf. Sci. 601, 1582 (2007).

10:40am SS1-ThM9 In-Situ Polarization and Structure of 4 and 10 Layer Epitaxial BaTiO₃ Films, *A.P. Baddorf*, Oak Ridge National Laboratory, *J. Shin, V.B. Nascimento*, University of Tennessee, *S.V. Kalinin*, Oak Ridge National Laboratory, *E.W. Plummer*, University of Tennessee

Ultrathin films of ferroelectric materials lose their ferroelectric properties due to the depolarizing field opposing the polarization. It is important to understand the limits and conditions limiting nanoscale ferroelectrics, which are being considered for a number of sensors, memories, and transistor devices. For $BaTiO_3$, ferroelectricity has previously been observed experimentally down to 12 layers and predicted by first-principles calculations in 6 layer films. Film environment and interfaces play a critical role in ferroelectric properties. We have grown BaTiO3 ultra-thin films $SrRuO_3$/$SrTiO_3$ using laser-MBE in high oxygen pressures (10 mTorr). The large 2.3% lattice mismatch in this system requires careful choice of growth conditions. For ultrathin films, RHEED oscillations and patterns during growth show that layer-by-layer growth of flat, highly strained films is possible. We report in-situ, ultrahigh vacuum characterization of epitaxial films using low energy electron diffraction (LEED I-V) and scanning tunneling spectroscopy (STS). Films produce sharp (1x1) LEED patterns, indicating a well-ordered tetragonal phase structure. Comparison of observed diffraction intensities for 4 and 10 layer films at 130 and 300 K with calculated intensities reveals a vertical displacement of the central Ti, corresponding to a polarization consistent with compressive strain. Structures and polarization change dramatically after exposure to small quantities of water. STS shows discontinuous jumps at +/- 2.5 V that may indicate polarization switching. Research was sponsored by the Division of Materials Sciences and Engineering and the Center for Nanophase Materials

Authors Index

Bold page numbers indicate the presenter