

Surface Science

Room 208 - Session SS1+MC-WeA

Oxide Surfaces, Interfaces and Defects

Moderator: R.L. Kurtz, Louisiana State University

2:00pm SS1+MC-WeA1 Metal/Metal-Oxide Interactions and Structures in Bulk Truncated and Thin Film Systems --The Theoretical View, *D.R. Jennison*, Sandia National Laboratories

INVITED

Using DFT with up to hundreds of atoms per slab unit cell, I use several sources to illustrate basic principles concerning metal-oxide surfaces, interactions with adspecies and metal overlayers, and ultrathin (<1nm) oxide films on metals and adsorption thereon: 1) Metal oxides vary greatly in relaxation to adsorbates, with those of alumina among the largest. This surface becomes so locally oxidizing that multiply charged metal adatoms can occur. 2) The interface between an oxide film and a basal-plane metal substrate can differ fundamentally. Most metals prefer O(1x1), but the noble metals prefer cations, which convert to a somewhat positive metallic layer with O-ions above. 3) Point defects can nucleate metal islands and alter growth and adhesion. However, common Fs and Vs centers destabilize metal dimers (the first step in nucleation), while another common defect, ad-OH, does the opposite. In fact, 1/3 ML of ad-OH on sapphire reverses the growth mode and more than doubles the adhesion of Cu metal. These results are simply due to geometry and electrostatics. 4) Ultrathin film adsorbate response depends on the substrate: While alumina on Ru is rather inert to a Pd overlayer, the film on Al(111) reacts strongly, drawing substrate metal into the oxide and extruding Al from the top to form a Pd/Al interface. Such is explained by cohesive energy differences between Al and Ru. 5) While complex mixed structures of oxides and metals cannot be predicted by simulation, proposals from STM data can be tested. In addition, model calculations expose basic factors such as interface preference, near-interface oxide film structure, and the resulting film stress, explaining the presence and variety of relief mechanisms. In this active field, examples, including experimental results, are drawn from alumina, magnesia, and titania. My valued collaborators are several. @footnote 1,2@ @FootnoteText@ @footnote 1@www.sandia.gov/surface_science/drj/. @footnote 2@Supported by US DOE.

2:40pm SS1+MC-WeA3 Ultrathin Fe Oxides on Cu(001): a Search for Half-Metallic Films, *R.H. Madjoe*, A.N. Koveshnikov, Louisiana State University; J. Karunamuni, University of South Carolina; R.L. Stockbauer, R.L. Kurtz, Louisiana State University

Half-metallic oxides such as CrO₂ and Fe₃O₄ may provide opportunities for new magnetic devices since their single spin orientation at the Fermi level gives rise to spin-dependent transport. However, these films are most often grown on oxide substrates which are not currently incorporated in GMR devices. We report a study of the electronic and geometric structures of Fe₃O₄ films grown on copper, which is currently used in commercial heterostructures. A broad array of techniques including ARUPS, NEXAFS, LEED and STM were used to characterize these films. They were grown by depositing Fe on Cu(001) at room temperature and oxidizing at 810K in 10⁻⁶ Torr O₂ ambient. The particular oxide phase that forms depends on the initial Fe thickness. For Fe films less than 2 ML thick, LEED and STM measurements show that oxidation produces an FeO(111) bilayer. The oxide forms long, narrow strips with two mutually-perpendicular orientations aligned along Cu[110] and [110]. Oxidation of thicker Fe layers give crystallites of Fe₃O₄(111) of micron dimensions, which are oriented 15° from the [010] directions and highly lattice-matched to the Cu substrate. Both core level and valence band photoemission data will be presented. Difference spectra show that the interfaces of these films have a metallic density of states at EF, unlike any of the bulk phases of iron oxide. Near-edge x-ray absorption fine-structure (NEXAFS) at both the oxygen K- and Fe L_{2,3}-edges will be presented in addition to magnetic linear and circularly-polarized dichroism (MLD, MCD) data. These data will be discussed in the context of the evolution of the electronic structure to that of thicker bulk-like oxide films.

3:00pm SS1+MC-WeA4 Low Temperature Microcalorimetric Heats of Adsorption and Sticking Probabilities of Metals on Oxide Surfaces, *D.E. Starr*, C.T. Campbell, University of Washington

Single crystal adsorption microcalorimetry is a powerful method to study the heats of adsorption of gaseous atoms or molecules onto single crystal surfaces. The technique has been utilized to study the energetics of metal

film growth from the initial stages of growth through the multilayer regime. Results for metal deposition onto metal oxide substrates all indicate an initial heat of adsorption much lower than the bulk heat of sublimation of the metal. This indicates a weaker interaction of the metal atoms with the substrate than with themselves, providing insights into the energetic driving force for the three dimensional islanding of the metal film in the submonolayer regime. Recent advances in this technique has allowed the first low temperature measurements (~ 160 K) to be performed. Low temperature results for the deposition of Pb onto a MgO(100) thin film grown on Mo(100) will be presented. These measurements have similar sensitivities to room temperature measurements. The changes in the heat of adsorption versus coverage from room temperature measurements to low temperature result from the kinetic factors governing the film morphology. In conjunction with the calorimetric measurements, the metals sticking probability as a function of coverage at a variety of temperatures allows kinetic parameters to be extracted from the model fit to the sticking probability curves. This results in deeper insights into the microcalorimetrically measured heats of adsorption.

3:20pm SS1+MC-WeA5 Electronic Structure of Grain Boundaries in TiO₂ from Ab-Initio Calculations, *Z. Mao*, S.B. Sinnott, E.C. Dickey, The University of Kentucky; R.F. Wood, Oak Ridge National Laboratory

It is well known that the properties of grain boundaries have important effects on the electronic and chemical properties of polycrystalline materials. In this work, we apply first principles electronic structure calculations to study the structure of TiO₂sub 2@ grain boundaries and compare the results to experimental data. Specifically, the density functional method within the local density approximation is used to determine the structure of several tilt grain boundary structures in TiO₂sub 2@. In addition, intrinsic defect formation energies at these boundaries are calculated by examining the stability of various individual defects within the bulk and at the grain boundary. These results provide information about the atomic basis for grain boundary space charge segregation and its dependence on grain boundary structure. This work is supported by the National Science Foundation (DMR-9976851).

3:40pm SS1+MC-WeA6 Surface Defects on MgO Thin Films: Formation, Detection, Electronic and Chemical Properties, *A.A. Kolmakov*, X. Lai, J.A. Stultz, D.W. Goodman, Texas A&M University

Surface defects play a significant role on metal oxide surfaces since they determine its electronic structure, chemical reactivity and adsorbate kinetics. There is great interest in studying surface defects on thin-film metal oxides to understand the properties of supported catalysts and gas sensing devices at the molecular level. Because of the low density of these oxide defects and sample charging, experimental studies of oxide surface defects still remain a challenging task. Using an ultrathin film deposition methodology and high surface sensitive capabilities of metastable impact electron spectroscopy (MIES), ultraviolet photoelectron spectroscopy (UPS) and temperature programmed desorption (TPD) along with scanning tunneling microscopy (STM), the properties of surface and near-surface defects were probed. A comparative study of morphology and electronic structure with reactivity of low-defect MgO(100) films was undertaken. Defect-ridden films exhibited occupied levels located ~2 eV above the top of the valence band, observed as a separate band in MIES, unlike defect-free thin films. This additional feature was attributed to the emission of electrons from point defects (F-centers) created on the surface and subsurface regions. Initially unseen in MIES, extended defects became detectable via NO titration. These defects manifest themselves as strong, reactive centers. MIES and TPD data indicate that at ~100 K, NO adsorbs dissociatively on surface defects and produces N@sub 2@O. Differences in electronic and chemical properties between these two films were further evidenced from their morphological differences as observed by STM.

4:00pm SS1+MC-WeA7 Metallic Electronic States on SrTiO@sub 3@ (110) Surface -- An In Situ Conduction Measurement, *H. Bando*, Electrotechnical Laboratory, Japan; Y. Ochiai, Ibaraki University, Japan; Y. Aiura, Electrotechnical Laboratory, Japan; Y. Haruyama, Himeji Institute of Technology, Japan; T. Yasue, University of Tsukuba, Japan; Y. Nishihara, Ibaraki University, Japan

In our previous works we detected metallic electronic states on the SrTiO@sub 3@ (110) surface after annealing in ultra high vacuum (UHV) at relatively low temperature, @<= 800 °C, based on a sharp Fermi edge detected by ultraviolet photoemission spectroscopy and finite zero-bias differential conductance by scanning tunneling spectroscopy. In order to verify the metallic feature of the surface as a macroscopic property, electric conductance is measured in situ. For the measurement, a sample holder is

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designed which enables both annealing in UHV by electron beam and 4-probe electric conduction measurement with uniform electric field. Conductance contributed by bulk is separated by measuring the decrease of total conductance by adsorption of oxygen at room temperature, which is supposed to modify only the surface electronic states. Surface conductance is deduced between 150 K to 300 K and showed a metallic feature. Comments will be presented on the effects of surface anisotropy and photo-induced carriers. Moreover, the surface conductance during exposure to oxygen is monitored in situ, and showed a reversible-like change depending on the oxygen pressure. This possibly evidences that the oxygen molecules which temporarily stay on the surface suppress the conduction by surface electrons.

4:20pm **SS1+MC-WeA8 First-Principles Calculations on Al@sub 2@O@sub 3@/TiC Growth and Interface**, *C. Ruberto, B.I. Lundqvist*, Chalmers University of Technology and Göteborg University, Sweden

First-principles calculations based on density-functional theory are performed to understand the first steps in the growth of alumina on TiC(111). The alumina/TiC interface is theoretically very interesting, being an example of interface between an oxide, ionic and insulating, ceramic and a covalent transition-metal ceramic with metallic and ionic character. The TiC(111) facet is furthermore a highly active and polar surface. Technologically, the interface is of high importance in wear-resistant cutting tools used in industrial high-speed applications. Different phases of alumina (mainly the @alpha@ and @kappa@ phases) are used as chemically-inactive coatings on cemented-carbide tools. These coatings are grown on TiC(111), TiN(111), or Ti(C,N)(111) through chemical-vapor deposition (CVD). It is known that the coating quality and phase content are determined by the nucleation on the substrate surface. For example, a region of @gamma@ alumina is sometimes observed between TiC and @kappa@ alumina. This work is the first step towards establishing a fundamental understanding of the interfacial structure and of the growth of alumina on TiC(111). This is done in several steps. We investigate the adsorption energies of the different atomic species present in the CVD reactor on the TiC(111) surface. The energetics for the different atomic configurations of an aluminum layer at 2/3 coverage on TiC(111)-O are studied and the observed structural stability is understood on the basis of bonding character. The influence of thermal lattice expansion is discussed. The stability and bonding character of a layer of stoichiometric Al@sub 2@O@sub 3@ in different structural configurations on TiC(111)-O are then examined. Finally, the structure and stability of all different atomic terminations of the @kappa@-Al@sub 2@O@sub 3@(001) and (00-1) surfaces, the preferred CVD growth direction, are presented and discussed.

4:40pm **SS1+MC-WeA9 Self-Diffusion in Ceria**, *C.L. Perkins, M.A. Henderson, G.S. Herman*, Pacific Northwest National Laboratory

Ceria, an oxygen storage material vital to the proper functioning of automobile three-way catalysts, is typically viewed as an anion conductor. In light of mounting evidence that in the prototypical oxide rutile TiO@sub 2@ the mobile species are Ti cations rather than O anions, the diffusivities of both cerium and oxygen in ceria were explored via temperature programmed static secondary ion mass spectrometry (TPSSIMS). The 500 Å thick CeO@sub 2@(111) film was heteroepitaxially grown by molecular beam epitaxy on a yttria stabilized zirconia substrate. Although high quality LEED patterns and Auger spectra free of signals from elements other than cerium and oxygen were obtained after just a few sputtering and annealing cycles, further cleaning was necessary to remove intense alkali and alkaline earth signals observed in SSIMS. The CeO@sub 2@(111) surface was slightly enriched in @super 18@O by first annealing the film in UHV at 830 K and then exposing the 130 K crystal to @super 18@O@sub 2@. TPSSIMS data in conjunction with temperature programmed desorption (TPD) data demonstrate that surface oxygen begins to diffuse into the bulk around 550 K. Physical deposition in an @super 18@O@sub 2@ background of submonolayer amounts of isotopically enriched cerium (@super 136@Ce) allowed the simultaneous study of the diffusivity of both cerium and oxygen. Surface cerium cations were found to be immobile with respect to diffusion into the bulk up to the highest temperature studied, 900 K.

5:00pm **SS1+MC-WeA10 Defect Characterization on MgO(100) Using Adsorption of Small Molecules**, *Z. Dohnálek, G.A. Kimmel, R.S. Smith, S.A. Joyce, B.D. Kay*, Pacific Northwest National Laboratory

MgO(100) films with controlled defect densities are grown epitaxially on Mo(100). The crystalline order is probed using both low energy electron diffraction (LEED) and the adsorption of small probe molecules such as N@sub 2@, Ar, CO, CH@sub 4@, H@sub 2@O, NH@sub 3@ and CH@sub 3@OH. Significant changes in the LEED beam profiles are observed for films

grown at various substrate temperatures, deposition rates, and film thicknesses. Thick films grown at high temperatures yield the sharpest LEED profiles. While the quality of the LEED pattern is related to the presence of morphological defects, it is difficult to quantify and characterize the defects by LEED alone. Temperature programmed desorption (TPD) of physisorbed molecules deposited at 20K reveals a wide distribution of binding sites on the highly-defective films. Analysis of the TPD spectra yields the binding energies and concentrations of these defect sites for various adsorbates. Both the LEED and TPD from the highest quality epitaxial films are indistinguishable from highly-ordered bulk MgO(100). Even on the best surfaces, a well resolved minority desorption channel related to defects is observed, thereby demonstrating the high sensitivity and quantitative nature of TPD in characterizing defects. * Pacific Northwest National Laboratory is operated for the Department of Energy by Battelle under Contract DE-AC06-76RLO 1830.

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