

Tuesday Morning, November 10, 2009

Surface Science

Room: M - Session SS1-TuM

Oxide Surfaces: Reactions and Structure

Moderator: R.L. Kurtz, Louisiana State University

8:00am **SS1-TuM1 UV Induced Work Function Change of Oxide Surfaces**, *S. Gutmann, M. Wolak, M. Conrad, M.M. Beerbom, R. Schlaf*, University of South Florida

The work function of conductive oxide thin films is an important parameter determining the band line-up at interfaces to active electronic materials in optoelectronic devices. The presented experiments aimed at the measurement of the work function of indium tin oxide (ITO), and nanocrystalline TiO₂ and ZnO thin films using photoemission spectroscopy. Traditionally, ultraviolet photoemission (UPS) is used to measure the work function of solid surfaces by means of the photoelectric effect. Such measurements are able to yield absolute work function values.

Our experiments showed that UPS measurements reduce the work function of oxide surfaces by up to 0.5 eV. This effect occurs within seconds, effectively preventing measurements of the 'true' work function of surfaces prior to UV exposure. A similar effect is observed when exposing oxide surfaces to x-ray doses typical for x-ray photoemission spectroscopy measurements. It was possible to quantify these effects through the use of low intensity XPS (LIXPS) based work function measurements, which allow a time-window sufficiently long for work function measurements without significantly influencing the work function. The experiments suggest that the work function reduction occurs through the hydroxylation of oxygen vacancies in the oxide surfaces by means of photochemical dissociation of adsorbed water molecules.

8:40am **SS1-TuM3 Low-energy Alkali Ion Scattering Studies of Bi₂Sr₂CaCu₂O_{8+δ}**, *R.D. Gann*, University of California, Riverside, *J. Wen, Z. Xu, G.D. Gu*, Brookhaven National Laboratory, *R.Q. Wu*, University of California, Irvine, *J.A. Yarnoff*, University of California, Riverside

The high-*T_c* cuprate BSCCO-2212 is investigated with low energy (0.5-10 keV) alkali ion scattering, which is an extremely surface-sensitive technique that can reveal compositional, structural and electronic information about a surface. Samples were cleaved at liquid nitrogen temperature in ultra-high vacuum, and time-of-flight spectroscopy was used to measure charge-resolved energy spectra of the scattered ions. Clean surfaces were shown to be terminated by BiO, and the inhomogeneous surface potential of the as-cleaved surface was revealed by the angular dependence of the neutralization. The effect on local potential due to adsorption of alkali and halogen species was ascertained by neutralization measurements and verified with density-functional theory. Deliberate damage induced by 500 eV argon sputtering revealed a gradual disordering of the surface as underlying metallic species diffuse upward, rather than layer-by-layer etching, as earlier SIMS studies have suggested. A detailed view of the surface termination opens the door for studies of other, similarly layered materials such as Bi₂Se₃.

9:00am **SS1-TuM4 Termination and Identification of Surface Species on the Magnetite (111) Surface Studied by Scanning Tunneling Microscopy**, *T.K. Shimizu, Y. Kim*, RIKEN, Japan, *M. Kawai*, RIKEN and University of Tokyo, Japan

Besides its magnetic properties, magnetite exhibits an interesting first order phase transition called the Verwey transition (*T_V*~120 K). Although there have been many atomistic investigation using scanning tunneling microscopy (STM) at room temperature (RT), the most stable structure of Fe₃O₄(111) has not been yet in complete agreement. By employing STM and scanning tunneling spectroscopy (STS) at 77 K, we have studied the Fe₃O₄(111) surface using a naturally grown single crystal. STM images show a hexagonal lattice with an approximately 0.6 nm periodicity, no remarkable difference from RT observations. Based on the comparison of STS with a theoretical calculations, this surface can be assigned to the Fe_{tet} termination, where the layer of Fe cations at the tetrahedral site terminates the crystal, supporting results of several early studies. In addition to these findings, we found two distinct features on the as-prepared surface. These features are considered to be the same species as those seen in the RT STM study [1] from the site and the bias dependence of their appearances. We were able to obtain direct evidence of their origin being water by intentionally adsorbing water both at 77 K and at RT, in agreement with previous predictions [1]. For instance, by injecting tunneling electrons into as-dosed intact water molecules at 77 K, we could induce reactions to one

of the originally observed species. In contrast to RT experiment, however, their diffusion requires much higher energy, which may be explained by the inefficient electron-phonon (e.g., OH stretching mode) coupling due to the smaller number of electronic states available near the Fermi level below the Verwey transition temperature.

[1] Sh. Shaikhutdinov and W. Weiss, *J. Mol. Catal. A: Chem.* 158, 129-133 (2000)

9:20am **SS1-TuM5 Scanning Tunneling Microscopy Investigation of the Vanadium Dioxide Surface and Its Related Metal-Insulator Transition (MIT)**, *W. Yin, P. Reinke, S. Wolf*, University of Virginia, *C. Ko, S. Ramanathan*, Harvard University

Vanadium dioxide (VO₂) is one of the most interesting thermochromic materials exhibiting a metal-insulator transition (MIT) close to room temperature (*T_{MI}* ≈ 340 K). This study presents an observation of the progression of the MIT with scanning tunneling microscopy and spectroscopy as a function of temperature with high spatial resolution. The high-quality VO₂ thin films used in this study were deposited on (0001) Al₂O₃ substrates using a sputtering technique. Electron tunneling current (conductivity) maps showed that the material surface was semiconducting before heating, and highly metallic above *T_{MI}*. The spatial distribution of bandgaps, semiconducting and metallic regions, is compared to the sample topography, and a model describing the progression of the MIT across the surface will be presented. In particular, the role of the chemical modification and reduction of the surface during heating will be discussed, and compared to the stability of the bulk phase. The surface was still partially metallic after cooling down but tended to recover its semiconducting nature over a long period of time. We attribute such irreversible surface electrical changes to the loss of oxygen and the strain relaxation in the VO₂ lattice. The spatial distribution of bandgaps indicates that the phase transition probably started from grain boundaries and the VO₂ surface exhibited an inhomogeneous behavior both above *T_{MI}* and after heat treatment.

9:40am **SS1-TuM6 The Adsorption and Reaction of Alcohols on Poorly Crystalline γ-Al₂O₃ Surfaces**, *J. Kwak, J. Szanyi, C. Peden*, Pacific Northwest National Laboratory

γ-alumina, one of the metastable 'transition' alumina structural polymorphs, is an important catalytic material both as an active phase and as a support for other catalytically active phases, with widespread applications ranging from petroleum refining to automotive emission control. As such, the bulk and surface structure of γ-alumina, and its formation and thermal stability have been and continue to be the subject of a considerable amount of research, including attempts to prepare model surfaces via the controlled oxidation of NiAl alloy single crystals. However, due to the low crystallinity and very fine particle size of γ-alumina, it is very difficult to apply well-established analytical techniques for determining its surface structures. Of particular importance for understanding the catalytic properties of γ-alumina, relating its surface structure to the origin of Lewis and Brønsted acidity has been of considerable interest and has been studied by solid state NMR and FTIR spectroscopies, and most recently by theoretical calculations. In this presentation, we describe recent studies using ultra-high resolution NMR spectroscopy as an especially useful probe of the γ-alumina surface structure, and its relevance to catalytic behavior. In particular, we correlate the NMR spectra with measurements of the adsorption and reaction of alcohols. In this way, we demonstrate a strong dependence of this chemistry on the presence of specific 5-coordinate Al³⁺ ions. These sites, in turn are a function of the dehydration temperature of the alumina material before use. From these correlations, we are able to explain a considerable number of prior observed phenomena.

10:40am **SS1-TuM9 The Growth and Structure of Ceria Islands on Cu(111)**, *F. Yang, J. Graciani, S. Senanayake, J.B. Park, D.J. Stacchiola, P.J. Liu, J. Hrbek, J.A. Rodriguez*, Brookhaven National Laboratory

Ceria-based catalysts are widely used for a number of catalytic reactions, such as the water gas shift reaction (CO + H₂O → H₂ + CO₂) or CO oxidation (CO + 1/2 O₂ → CO₂). Recently, it has been reported that ceria nanoparticles supported on Au(111) are much more efficient for the water gas shift reaction than the oxide or metal alone. In this work, we investigate the CeO_x/Cu(111) system as a model for Cu-CeO₂ water-gas shift catalysts. Using scanning tunneling microscopy (STM), we study the nucleation and growth of ceria islands on the Cu(111) surface. Ce is vapor-deposited on Cu(111) under an atmosphere of O₂ (~ 1 × 10⁻⁷ Torr) at different temperatures (300-600 K). We show how the geometric structures of ceria islands could be changed by altering the growth kinetics. We also show the evolution of the morphology when the CeO_x/Cu(111) surface interacts with CO or H₂O. Through an interplay with density functional theory (DFT) and

X-ray photoelectron spectroscopy (XPS), the structure of supported ceria islands will be described.

11:00am **SS1-TuM10 Morphology and Electronic Structure of Ultrathin Oxide Films on Pt₃Ti(111)**, *M. Moors, S. Le Moal, C. Becker, K. Wandelt*, University of Bonn, Germany

TiO₂ supported metal catalysts are known to have interesting catalytic properties, e.g. for oxygen reduction of water in fuel cells and for CO hydrogenation. The formation of titanium oxides on Pt-Ti alloy surfaces is one promising approach to develop new TiO₂ based model catalysts. In this work the crystallographic and electronic structure as well as the surface composition of ultrathin titanium oxide films grown on a Pt₃Ti(111) single crystal surface have been investigated as a function of oxidation temperature (700 K to 1000 K) and oxygen exposure (up to 9000 L) using Low Energy Electron Diffraction (LEED), Ultraviolet Photoelectron Spectroscopy (UPS) and Auger Electron Spectroscopy (AES). The composition of the titanium oxide films formed on this alloy surface strongly depends on the preparation conditions. From AES and LEED measurements two different stable oxide phases have been identified at high temperatures (above 900 K), depending on the oxygen exposure. At lower oxygen exposures (below 135 L) the most stable structure is a quasi-hexagonal one ($a = 3.35 \text{ \AA}$, $b = 3.25 \text{ \AA}$, $\alpha = 124^\circ$) rotated by 4° with respect to one of the substrate symmetry axes. The $p(2 \times 2)$ pattern, which is attributed to the Pt₃Ti(111) substrate, is still visible after this mild oxidation; suggesting that some areas of the substrate remain unoxidized. At higher oxygen exposures (between 220 L and 9000 L) the predominant structure is a commensurate hexagonal structure ($a = 3.20 \text{ \AA}$) rotated by 4° with respect to one of the substrate symmetry axes. In this case the $p(2 \times 2)$ substrate structure is no longer visible. Apart from these two stable structures, several additional LEED patterns have been observed, which are related to metastable oxide structures. However, this great diversity of LEED patterns is not reflected in the UPS measurements. Comparing the clean Pt₃Ti(111) surface with Pt(111) shows a significant broadening of the Pt related intensity between 1 and 4 eV as well as the appearance of a strong Ti related signal around 6 eV. For the clean Pt₃Ti(111) surface a work function of 5.02 eV has been determined. Oxidizing the alloy leads to additional peaks at a binding energy of 5.5 and 7.5 eV. The work function of the oxidized surface is increased by 0.3 eV related to clean Pt₃Ti(111). Remarkably, neither the spectral shape nor the work function significantly depends on the temperature and oxygen pressure used during oxidation.

11:20am **SS1-TuM11 Facile C-H Bond Cleavage of Propane on a PdO(101) Thin Film**, *J.F. Weaver, C. Hakanoglu, S.P. Devarajan, A. Minter*, University of Florida

Palladium oxide (PdO) is an excellent catalyst for the oxidation of alkanes under oxygen-rich conditions, but difficulties in preparing well-defined surfaces have hindered fundamental studies of PdO surface chemistry. We have recently found that a high-quality PdO(101) thin film can be grown on Pd(111) in ultrahigh vacuum by oxidizing the metal at moderate temperature using an oxygen atom beam. In this talk, I will discuss recent results showing that propane adsorbs into a strongly-bound molecular state on PdO(101) and undergoes facile C-H bond cleavage below 200 K. The adsorbed hydrocarbon fragments are completely oxidized by the PdO surface above about 400 K, yielding gaseous CO₂ and H₂O during temperature-programmed experiments. From measurements of product yields as a function of the surface temperature, we show that the initial C-H bond cleavage of propane on PdO(101) occurs by a precursor-mediated mechanism with a negative, apparent activation energy, and present evidence that the strongly bound molecular state serves as the precursor to the initial dissociation. We suggest that a donor-acceptor interaction between a C-H bond(s) of the propane molecule and a coordinatively unsaturated Pd atom enhances the binding of propane on PdO(101), beyond that expected for physisorbed molecules, and facilitates C-H bond activation. Finally, I will summarize recent experimental and computational results which show that CH₄ and H₂ molecules also interact strongly with PdO(101) through dative bonding. The activation of propane on PdO(101) is analogous to alkane reactions with mononuclear transition metal compounds for which alkane sigma complexes act as key intermediates.

11:40am **SS1-TuM12 Investigation of Oxygen Embedment and Surface Restructuring on the Cu(100) Surface by Density Functional Theory Calculations**, *M. Lee, A. McGaughey*, Carnegie Mellon University, *J. Ren, J.C. Yang*, University of Pittsburgh

When the oxidation of a Cu(100) surface reaches 0.5 monolayer (ML) oxygen coverage, the surface structure transforms into the missing-row reconstruction. With further oxygen exposure, cuprite (Cu₂O) islands nucleate and then grow both into and along the surface. To investigate the early stages of Cu(100) oxidation, we apply density functional theory calculations to study the oxygen embedment into the surface using the nudged elastic band (NEB) method. We find that as the surface oxygen

coverage increases on the unreconstructed Cu(100) surface, the energy barrier for embedment decreases and the oxygen embedment is energetically favorable at coverages of 0.75 ML and 1.0 ML. At 0.5 ML coverage, the embedment energetics vary with surface morphology [$c(2 \times 2)$, missing-row reconstruction, and $c(2 \times 2)$ with 0.25 ML disordered vacancy structures], but in all cases the embedment is not energetically favorable. At 0.625 ML coverage, however, the oxygen embedment is favorable and we investigate the energetics for embedment into the missing row reconstruction through the missing row and alternate paths. We find that oxygen embedment through the missing row is more probable. We predict that oxygen sub-surface diffusion will occur because the energy barrier is comparable to that for surface diffusion. To study the intermediate states between the missing-row reconstruction and cuprite island nucleation, we are investigating various combinations of on- and sub-surface oxygen adsorbed structures by DFT calculation. We find that an additional oxygen molecule plays a role in the surface restructuring not only morphologically but also energetically for the unreconstructed Cu(100) surface. We are using a similar methodology to investigate the role of the additional oxygen molecule for surface restructuring on the missing-row reconstructed surface.

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