

# Monday Afternoon, October 29, 2012

## Oxide Heterostructures-Interface Form & Function

### Focus Topic

Room: 7 - Session OX+SS+TF+MI-MoA

## Chemistry of Oxide Surfaces and Interfaces

Moderator: M. Engelhard, EMSL, Environmental Molecular Sciences Laboratory

2:00pm **OX+SS+TF+MI-MoA1 Investigation of Al<sub>2</sub>O<sub>3</sub> Nanostructure Surfaces Using Charge Optimized Many Body Potentials**, D.E. Yilmaz, T. Liang, S.B. Sinnott, S.R. Phillpot, University of Florida

Aluminum oxide nanostructures have drawn attention due to their interesting physical and optical properties. In particular, photoluminescence peaks for these systems are attributed to oxygen vacancies and surface effects. Here, we apply third-generation Charge Optimized Many Body (COMB) potentials for the Al-Al<sub>2</sub>O<sub>3</sub> system to investigate the properties of Al<sub>2</sub>O<sub>3</sub> nanoparticle surfaces. In particular, the elastic properties and local atomistic strain distribution of nanoparticles with a range of sizes are determined, and the corresponding vibrational spectra are determined. The effect of oxygen vacancies and adsorbed surface atoms on the local strain and vibrational spectra are also determined. This work is supported by the National Science Foundation (DMR-1005779).

2:20pm **OX+SS+TF+MI-MoA2 Manipulating Ferroelectric Surfaces for Direct NO<sub>x</sub> Decomposition**, M.W. Herdich, A. Kakekhhani, S. Ismail-Beigi, E.I. Altman, Yale University

Current technology for removing nitrogen oxides from engine exhausts relies on nearly stoichiometric air to fuel ratios. Under these conditions, the concentrations of CO and unburned hydrocarbons in the exhaust stream are high enough to efficiently remove adsorbed oxygen from the platinum based catalysts in catalytic converters, ensuring that the catalysts do not become saturated with adsorbed oxygen. Direct catalytic decomposition of NO<sub>x</sub> to N<sub>2</sub> and O<sub>2</sub> in the presence of excess O<sub>2</sub> would eliminate the need for reducing species in automobile engine exhaust streams, allowing these engines to be run more efficiently. We have been investigating the potential of ferroelectric supports to modify the behavior of supported layers to enable direct NO<sub>x</sub> decomposition. Our approach involves first principles density functional theory and surface science techniques. Using both approaches we have investigated the interactions of N, O, and NO with bare ferroelectric lead titanate surfaces and surfaces modified to expose catalytic layers, in particular Ru oxides. Theory indicates that the behavior of the PbTiO<sub>3</sub> surface towards these species is sensitive to the polarization direction and termination of the ferroelectric and that stable RuO<sub>2</sub>-terminated surfaces can be created by manipulating the termination of the substrate. Experiments take advantage of plasma sources that allow the behavior of O and N atoms to be studied individually and epitaxial growth to manipulate the termination of the ferroelectric support. Favored reaction pathways are assessed using theory and temperature programmed desorption and related mass spectrometry methods.

2:40pm **OX+SS+TF+MI-MoA3 Catalyst Synthesis by Atomic Layer Deposition**, P.C. Stair, Northwestern University & Argonne National Laboratory **INVITED**

Atomic Layer Deposition (ALD) has enormous potential for the synthesis of advanced heterogeneous catalysts with control of composition and structure at the atomic scale. The ability of ALD to produce conformal oxide coatings on porous, high-surface area materials can provide completely new types of catalyst supports. At the same time ALD can achieve highly uniform catalytically active metal and oxide phases with (sub-) nanometer dimensions.

Vanadium oxide species supported on high surface area oxides are among the most important catalytic materials for the selective, oxidative conversion of hydrocarbons to useful chemicals. In our laboratory ALD has been used to synthesize both the catalytic vanadium oxide and the supporting oxide on both high surface powders and anodic aluminum oxide (AAO) nanoliths. These materials have been characterized by SEM, XRF, ICP, UV-Vis absorption spectroscopy, Raman spectroscopy and evaluated for the oxidative dehydrogenation (ODH) of cyclohexane.

More recently we have studied the synthesis of supported metal particles and developed what we call "ABC-type" ALD in which metal nanoparticles and support materials are grown sequentially in each ALD cycle. This method makes possible the synthesis exceptionally small particles, ca. 0.5 nm. Using additional ALD support layers at the conclusion of the growth, the metal particles can be stabilized against sintering while still remaining

active at high temperatures and reaction conditions. Moreover, the catalysts resist coke formation which is a leading cause of catalyst deactivation. These properties are imparted as a result of anchoring step and edge atom sites while leaving facet sites open for catalysis.

3:40pm **OX+SS+TF+MI-MoA6 Energy Alignment at Organic/Oxide Interfaces: The Influence of Adsorption Geometry and Chemical Bond on Interface Dipole**, S. Rangan, C. Ruggieri, S. Coh, R.A. Bartynski, K. Chitre, E. Galoppini, Rutgers University

The lack of control of the energy alignment at the interface between an organic layer and an oxide substrate remains a limitation to the performance of promising technologies such as dye sensitized solar cells, organic light emitting diodes or organic thin film transistors. The energy alignment depends not only on the choice of the starting materials, but also on more subtle parameters such as oxide surface termination or defects, and molecular layer preparation mode.

In an effort to disentangle the different aspect of the interface of an organic/oxide system, we have studied simultaneously the adsorption geometry and the energy alignment of the Zn(II) tetraphenylporphyrin (ZnTPP) molecule on the TiO<sub>2</sub>(110) and ZnO(11-20) surfaces. Two approaches have been pursued: 1) in-situ evaporation of the ZnTPP on a clean oxide surface prepared in ultra-high vacuum resulting in weakly bound multilayers or monolayers 2) ex-situ sensitization in a solution of ZnTPP derivative, modified with COOH anchoring group for chemisorption at the oxide surface.

Scanning tunnel microscopy has been used to characterize the clean oxides and the ZnTPP adsorption modes. X-ray photoemission, ultra-violet photoemission and inverse photoemission spectroscopies have allowed the exploration of both occupied and unoccupied states of the electronic structure, resulting in the full characterization of the energy alignment at the surface as a function of the molecular overlayer thickness. The electronic transport gap, obtained from the latter experimental techniques has also been compared to the optical gap obtained from reflection electron energy loss spectroscopy, thus allowing the characterization of bound excitonic states.

The effect of the ZnTPP/oxide interface preparation, as well as the effect of the oxide substrate on the energy alignment will be presented. The discussion will be extended to metallic substrates such as Ag(100) and Au(111) surfaces

4:00pm **OX+SS+TF+MI-MoA7 Energy-Level Alignment at Organic/Oxide Interfaces**, M.T. Greiner, Z.-H. Lu, University of Toronto, Canada **INVITED**

Oxide/organic interfaces play an important role in many organic electronic device designs. Oxides are frequently used as buffer layers to tune the energy-level alignment between electrodes and organic semiconducting layers, and thus allow for efficient hole/electron injection. As per the 'integer charge-transfer' (ICT) model, energy-level alignment at electrode/organic interfaces is governed by the electrode's Fermi level and the organic molecule's oxidation/reduction potential. While the ICT model was originally proposed for organic/organic interfaces, it also applies to a broad range of transition metal oxides. In this presentation we will discuss the energy-level alignment (ELA) of several organic semiconductors with transition-metal oxides. We will show that ELA is primarily governed by an oxide's work function, and that ELA is relatively insensitive to oxide electronic structure. As transition metal oxides can exhibit a wide range of work functions (~ 2 - 7 eV), and can possess a wide range of electronic properties (p-type to n-type) they are very versatile materials for use in organic electronics. We will their properties—such as work function and electronic structure—can best be utilized for use as buffer layers in organic light-emitting diodes and organic photovoltaics.

4:40pm **OX+SS+TF+MI-MoA9 Variable Kinetic Energy XPS of the Buried P3HT/ITO Interface**, M.T. Brumbach, Sandia National Laboratories, J.C. Woicik, National Institute of Standards and Technology

The characterization of buried interfaces is difficult and often has to be performed by post-processing methods where the interface is revealed, disturbed, and possibly altered by environmental exposure. Variable kinetic energy X-ray photoelectron spectroscopy (VKE-XPS) offers the ability to tune the depth of analysis while the use of hard X-rays allows for a deeper analysis. The combination of variable energy hard X-rays for XPS (HAXPES) allows for systematic evaluation through a buried interfacial region. An important inorganic/organic interface for use in organic photovoltaic devices is the poly(3-hexylthiophene) (P3HT) interface with indium tin oxide (ITO). In this work P3HT/ITO buried interfaces were examined using X-ray energies from 2.2-3.9 keV. The ITO surface was

additionally prepared using different pretreatment conditions. The P3HT film protected the ITO surface from adventitious adsorbents and allowed for sensitivity to the buried ITO surface. Robust peak fitting parameters were obtained to model the O 1s and In 3d lineshapes. The deconvolution of these lineshapes allowed for the clear identification of a surface layer on the ITO which is oxidized to a greater extent than the underlying bulk ITO. The surface oxide layer, composed of indium oxide and indium hydroxide, is deficient of oxygen vacancies and would therefore be expected to act as an insulating barrier on the ITO surface. Peak fitting conditions allowed for an estimation of the thickness of this insulating layer. Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

5:00pm **OX+SS+TF+MI-MoA10 Organic Molecules Adsorbed on the ZnO(10-10) Surface: An Infrared Reflection Absorption Spectroscopy Study.** *M. Buchholz*, Karlsruhe Institute of Technology, Germany, *H. Noei*, *Y. Wang*, Ruhr University Bochum, Germany, *A. Nefedov*, *Ch. Wöll*, Karlsruhe Institute of Technology, Germany

Except for gold, every metal forms an oxide on its surface when exposed to the ambient atmosphere. The understanding of chemical processes taking place on metal oxide surfaces are thus of crucial importance. One of the most important oxides is ZnO. As a result of its semiconducting and optical properties, this material is used in many applications such as gas sensors, thin film solar cells, as well as in photocatalysis and photooxidation[1]. The important surfaces of ZnO are the polar Zn- or O-terminated ZnO(0001) and ZnO(000-1) as well as the mixed-terminated ZnO(10-10) surface. The latter is the dominating surface for ZnO powder particles and energetically most favorable.

Here we report on the adsorption of formic acid and maleic anhydride (MA) molecules on the mixed-terminated ZnO(10-10) surface. Formic acid is a good model molecule for understanding the anchoring of carboxylic dye molecules in dye-sensitized solar cells. The choice of MA is motivated by the importance of the industrial process where MA is hydrogenated using Cu/ZnO catalysts. The identification of the reaction mechanism requires the identification of intermediates using IR-spectroscopy[2].

In last decades numerous IR investigations of oxide powders have been reported. An unambiguous assignment of the features present in the complex powder IR spectra, however, is only possible on the basis of reference data recorded for well-defined systems, e.g. surfaces of single crystals with defined orientation. Unfortunately, Infrared Reflection Absorption Spectroscopy (IRRAS) studies of molecular adsorbates on oxide single crystals, and, in particular on ZnO, are extremely scarce due to the fact that the sensitivity of IRRAS to adsorbate vibrations is two orders of magnitude lower for oxides than for metals. Whereas in case of TiO<sub>2</sub> recently with improved experimental setups adsorbate vibrations have been observed for a number of cases[3], to our knowledge molecular vibrations on clean ZnO single crystal surfaces have not yet been reported. With our novel UHV-IRRAS setup[4] high-quality IR spectra of different molecular adsorbates on ZnO(10-10) could be recorded in a routine fashion. In this presentation the obtained results will be presented and discussed.

M. Buchholz gratefully acknowledges the financial support from the Helmholtz Research School "Energy-Related Catalysis".

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[4] Y. Wang, A. Glenz, M. Muhler, C. Wöll, *Rev. Sci. Instrum.* **2009**, 80, 113108-113106.

5:20pm **OX+SS+TF+MI-MoA11 In Situ Interface Analysis of Self-Assembled Monolayers on Metal Surfaces at High Water Activities by Means of a PM-IRRAS/QCM-Setup.** *I. Giner*, *M. Maxisch*, *G. Grundmeier*, University of Paderborn, Germany

Aluminum and its alloys are widely used as engineering material and in a wide range of applications ranging from the aviation industry to the automotive and construction industries. As almost all engineering metals, aluminum under ambient conditions is covered by a native oxide film which alters significantly its surface physical and chemical properties. For corrosion protection and adhesion promotion, oxide covered aluminum surfaces are coated with organic films. Ultra-thin films or even monomolecular layers of organic acids like self-assembled monolayers (SAMs) of organophosphonic and organocarboxylic acids have been investigated as new advanced interfacial layers for aluminum alloys.<sup>1</sup> However, the stability of the self-assembled monolayers under environmental conditions is an aspect for technical applications. Different

studies concerning to the stability and structure of the self-assembly monolayers under high humidity's conditions have been performed.<sup>2</sup> These studies revealed that the organic film decreased the amount of interfacial water layer but cannot prevent the water diffusion through the monolayer.<sup>3</sup> The aim of the present work is to establish an in-situ setup combining quartz crystal microbalance (QCM) and PM-IRRAS to study the chemistry of passive films and adsorbed organic monolayers at high humidity. The metal coated quartz was used as the reflecting substrate for the PM-IRRAS measurement. Thereby, the structure of the monolayer, the amount of adsorbed water and the chemical state of the surface layer in the presence of an adsorbed water layer could be analysed in-situ. The surface hydroxyl density prior to organic molecule adsorption was adjusted by means of low temperature Ar- and H<sub>2</sub>O- plasma treatments. Adsorption studies of H<sub>2</sub>O on nonadecanoic carboxylic acid (NDA) monolayer modified surfaces in comparison to bare oxide covered aluminum surfaces showed, that the NDA monolayer leads to a reduced amount of adsorbed water based on the inability of water to form hydrogen bonds to the low energy aliphatic surface chemistry. Moreover the kinetics of chemisorption of water indicated by the oxyhydroxide peak growth at SAM/metal interfaces could be significantly inhibited. Furthermore, it is noticeable that interfacial carboxylate group coordinatively bound the oxide as well as the orientation of the NDA monolayer is not affected by the adsorption of several monolayers water. *Bibliography* 1. Thissen, P et al. *Langmuir* **2010**, 26, (1), 156-164 2. Thissen, P et al. *Surface & Coatings Technology* **2010**, 204 (21-22), 3578-3584. 3. Maxisch, M et al. *Langmuir* **2011**, 27 (10), 6042-6048

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