Monday Morning, October 19, 2015

Surface Science
Room: 113 - Session SS+AS+EN-MoM

Synthesis, Structure and Characterization of Oxides
Moderator: Sylvie Rangan, Rutgers, the State University of New Jersey

8:20am SS+AS+EN-MoM1 Oxygen Uptake on Rh(111), *Daniel Killelea, J. Derouin, R.G. Farber*, Loyola University Chicago
Rhodium surfaces are of high utility for the partial oxidation of small molecules. We present results from a study of the uptake of gas-phase oxygen atoms on the Rh(111) surface. A combination of temperature programmed desorption (TPD), Auger electron spectroscopy (AES), and scanning tunneling microscopy (STM) were used to determine the total amount of oxygen, the oxygen surface coverages, and the surface structures, respectively. Our findings suggest that oxygen atoms are readily incorporated in to the near-surface region on Rh(111) while retaining low oxygen surface coverages and structures. We further studied how the surface changes when the subsurface oxygen atoms emerge to the surface. These finding provide insight to the formation of bulk oxides, and show that high-coverages of oxygen are not necessary for absorption of oxygen into the selvedge.

8:40am SS+AS+EN-MoM2 Formation of Subsurface Oxygen and Surface Oxides on Ag(111) by Atomic Oxygen, *Jonathan Derouin*, R.G. Farber, D.R. Killelea*, Loyola University Chicago
Understanding the interaction of oxygen with transition metal surfaces is important in many areas including corrosion and catalysis. The oxygen/silver system in particular has been studied extensively both experimentally and theoretically. Interest is driven largely by the role of silver in two widely used industrial reactions: the epoxidation of ethylene to produce ethylene oxide and the partial oxidation of methanol to produce formaldehyde. In addition, the oxygen/silver system can serve as a model for the dissociative chemisorption of diatomic molecules on close packed metal surfaces. Despite extensive research, the oxygen/silver system is still not well understood. To better understand this system, we use UHV-STM, AES and TPD to study the adsorption of atomic O on an Ag(111) crystal. Atomic O is generated by thermally cracking molecular O. By varying the power of the thermal cracker we are able to change the flux of atomic O reaching the Ag surface. Higher atomic O fluxes produce O structures which desorb at significantly higher temperatures than structures produced with lower O fluxes. We then use UHV-STM to further characterize the various oxide structures produced.

9:00am SS+AS+EN-MoM3 Surface and Bulk Properties of Pure and Mixed Titania, *Matthias Batzill*, University of South Florida **INVITED**
Titanium oxide in its different polymorphs remains a model system for structure property relationships in simple oxides. In this talk we address issues related to both the bulk and the surface properties of TiO2. Measuring the photocatalytic activity of anatase- and rutile- epitaxial films we conclude that charge carriers excited deeper in the bulk contribute to the surface photocatalytic activity for anatase compared to rutile [1]. This difference may be an important factor for explaining the generally higher photocatalytic activity of anatase-TiO_2. In the second part of the talk, surface properties are presented on the example of rutile $TiO_2(011)$. The (011) surface orientation is less frequently studied compared to the (110) surface. Under UHV-conditions the (011) surface reconstructs into a complex 2x1 structure. We investigate the stability of this reconstruction under chemical adsorption. We find that for strongly adsorbing molecules the surface restructures to enable stronger adsorption. We show that this restructuring is strongly anisotropic resulting in quasi-1D adsorbate structures [2]. The instability of the rutile $TiO_2(011)$-2x1 surface may also be exploited for the formation of unique mixed oxide surfaces. This we demonstrate with iron oxide, which forms an ordered mixed TiFeOx surface oxide layer. Such mixed oxide surface may also form by impurity segregation from the bulk and thus may be a common surface structure in Fe-doped TiO_2.
[1] "Why is anatase a better photocatalyst than rutile? - Model studies on epitaxial TiO_2 films" T. Luttrell, S. Halpegamage, J.G. Tao, A. Kramer, E. Sutter, M. Batzill Sci. Rep. 4, 4043 (2014).

[2] "Adsorbate Induced Restructuring of $TiO_2(011)$-(2×1) Leads to One-Dimensional Nanocluster Formation" Q. Cuan, J. Tao, X.Q. Gong, M. Batzill Phys. Rev. Lett. 108, 106105 (2012).

9:40am SS+AS+EN-MoM5 Characterizations of Non-polar Polar Interfaces: Cr_2O_3 on ZnO (0001) and (000-1), *Xiaodong Zhu, M.D. Morales-Acosta, J. Shen, F.J. Walker, J. Cha, E.I. Altman*, Yale University
The growth of non-polar Cr_2O_3 on oppositely poled ZnO surfaces was characterized to determine how the polar substrate influences the properties of the non-polar film. Photoelectron spectroscopy (XPS and UPS), electron diffraction (RHEED and LEED), High-resolution transmission electron microscopy (HRTEM), X-ray diffraction (XRD) and X-ray reflectivity (XRR) have been performed to determine the growth mode, film quality and interfacial electronic properties are influenced by the substrate polarization. The growth is 2D; however, the films appear initially disordered on both substrates. With increasing film thickness, the films ordered with a well-defined epitaxial relationship. The HRTEM and XRD/XRR results for thicker films confirm a clear interface and well-defined lattice structure near the interface and throughout the film, indicating that above a critical thickness the entire film reorganizes into an ordered structure. The polar interfaces show a small but noticeable band offset that decayed with increasing film thickness. Statistical analysis of UPS valence band spectra revealed an enhanced density of states near the Fermi level for Cr_2O_3 on the positive surface consistent with stabilization of the positive interface by charge transfer; in contrast, no significant valence band differences were observed between bulk Cr_2O_3 and thin Cr_2O_3 thin layers on the negative surface. The results will be compared with those obtained for ZnO/Cr_2O_3/ ZnO (0001) and (000-1) to determine if the interfacial properties are sensitive to how the interface is formed.

10:40am SS+AS+EN-MoM8 Exploring Iron Oxide Clusters and Films Supported on HOPG with HREELS and AES, *Joel Langford*, University of California, Irvine, *F. Rosner*, Technical University of Munich, Germany, *J. Kwon, J.C. Hemminger*, University of California, Irvine
We are using High Resolution Electron Energy Loss Spectroscopy (HREELS) and Auger Electron Spectroscopy (AES) to investigate nanoclusters and films of iron oxide supported on highly oriented pyrolytic graphite (HOPG). For the films, two AES oxidation profiles were generated by annealing in oxygen. One profile was at a constant sample temperature of 500 K with varying exposure, the other by varying sample temperature while keeping exposure at a constant 1000 L. Both oxidation profiles saturate at an AES O/Fe ratio of 1.2. This ratio is below the O/Fe ratio of magnetite (Fe_3O_4), and hematite (Fe_2O_3) indicating incomplete oxidation of the film. Additional evidence for incomplete film oxidation comes from the absence of Fuchs-Kliewer phonons in the HREEL spectra. For the nanoclusters we are investigating two systems; polydispersed iron oxide nanoclusters on HOPG, and platinum nanoclusters supported on iron oxide nanoclusters. The polydispersed nanoclusters are more susceptible to oxidation than the film as evident by the higher AES O/Fe ratio and the presence of Fuchs-Kliewer phonons in the HREEL spectra. The platinum nanoclusters are synthesized on the iron oxide nanoparticles by an ex-situ photodeposition technique and therefore adventitious carbon is adsorbed prior to transfer into the UHV chamber. To remove the adventitious carbon we annealed in oxygen at a sample temperature of 1000 K. HREEL spectra show that the annealing procedure removes adventitious carbon because of the absence and appearance of a CO resonance before and after cleaning, respectively. HREEL spectra after low temperature CO adsorption and as a function of subsequent anneal temperature will be presented.

11:00am SS+AS+EN-MoM9 Computational Materials Design®: Ionic Conduction in Rare-Earth-Metal Oxides from the First Principles-based Studies, *Susan Aspera, M. Sakaue, M. Alaydrus, T.P.T. Linh, N.H. Linh, H. Nakanishi*, Osaka University, Japan, *H. Kasai*, Akashi College, Japan
Solid oxide fuel cells (SOFC) have been one of the most promising technologies to tap alternative sources of energy. This technology utilizes abundant fuel materials such as H_2, CH_4 and other hydrocarbon materials to lessen our dependence on non-renewable fossil fuels that are nearly depleting. It takes into advantage the efficiency brought about by high kinetics of reaction at the electrolyte sides occurring at high working temperature. With this, ceramic based materials are often used as electrolyte and electrode materials. However, the working temperature of SOFCs is often too high (700°C to 1000°C). This limits the application of SOFCs and consequently high cost of producing durable materials for high working temperature. Recently, research related to this technology focuses on materials that work at intermediate temperature (IT-SOFC). This entails

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* Morton S. Traum Award Finalist

finding/designing materials that have high ionic conductivity at IT-SOFC working temperature.

Recent developments in computational simulation techniques, coupled with the rapid progress in computer efficiency, make first principles-based COMPUTATIONAL MATERIALS DESIGN (CMD®) a relevant field in the world of surface science and condensed matter physics. In this scheme, quantum mechanical calculations are performed to design promising materials and, understand the necessary mechanisms for the realization of an efficient technological device. Here, we employed the CMD® process and density functional theory-based analysis to study the atomic and electronic properties of several rare-earth-metal oxides (Pr_2NiO_2, La_2GeO_5, $LaGaO_3$ and CeO_2) which has potential application in IT-SOFC. These materials are known to have different structures according to symmetry, and the mechanism by which O ion conducts, i.e. via oxygen vacancies (O_{vac}) migration or O interstitial migration. The O ion migration path is dependent on the structure of the material, and the corresponding activation energy barrier for oxygen ion migration (E_{ac}) is affected by the concentration of O_{vac} and the presence of dopants, for O ion conduction via vacancies. In most of these systems, dopants with the same ionic radius as the host materials create high probability for O_{vac}, which then affects ionic conductivity, and the E_{ac} is found to be least for dopants with ionic radius near to that of the host material. Furthermore, as ionic migration is sensitive to the atomic structure, E_{ac} is party due to the structural alteration brought about by the presence of impurities such as dopants and creation of heterostructure interfaces. With these understanding, we can comment on the methods by which ionic conductivity can be enhanced in these materials.

11:20am **SS+AS+EN-MoM10 Modeling and Characterization of Exemplar Sealing Glasses to Develop Chemistry-Structure-Property Relationships**, *Michael Brumbach*, *T. Zeitler, T. Alam, M. Rodriguez, L. Criscenti, M. Kalan, A. Mirabal, D. Bencoe, K. Ewsuk*, Sandia National Laboratories

The performance of joining materials in many applications, such as glass-to-metal seals in solid oxide fuel cells and medical devices, require improvements in glass properties for greater reliability. In this work, simple sealing glass compositions have been used to develop experimentally-validated molecular models. The goal is to understand glass chemistry and structure such that modeling can be used to guide glass design, for manufacturability, and optimized performance. The coupled modeling and experimental work will be discussed.

Technological glasses are used in many applications where inorganic joining is required. Applications of joining glasses include glass in glass-to-metal seals (in solid oxide fuel cells or medical components), glass-bonded ceramics (such as debased aluminas), and low temperature co-fired ceramic (LTCC) packaging for microelectronics. For these applications, well-controlled processing conditions and high reliability in the end-product are of paramount importance. To better understand materials performance and reliability our objective is to develop experimentally-validated simulation tools to predict and control glass chemistry-structure property relationships. These tools will be used to predict structure-function relationships in bulk glasses and at joining interfaces.

Results from experimental characterization of several barium aluminosilicate glasses will be discussed. Solid-state NMR, lab-based and synchrotron X-ray scattering, and EXAFS have been used to determine structural characteristics of the exemplar glasses. Comparison of experimental results to molecular dynamics modeling of the three-component glass will be presented. Additional simulations of glass properties and comparisons to measurements will also be discussed.

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