

# Friday Morning, November 1, 2013

## Surface Science

Room: 201 A - Session SS-FrM

### Oxides and Semiconductors: Structure and Reactivity

Moderator: G.A. Kimmel, Pacific Northwest National Laboratory

#### 8:20am SS-FrM1 Oxidation of Pd Supported on Au(111) and Single Crystal ZnO Supports, *J. Lallo, M. Batzill*, University of South Florida

Supported palladium catalysts are involved in many important catalytic reactions, such as steam reforming of methanol and methane combustion. Palladium oxide has been discovered to play an important role in these reactions, and the conditions and mechanisms involved for PdO formation are of great interest. In this work we investigate the role of substrates in palladium oxidation. Thin films of Pd, < 10nm, are grown on Au(111) and different crystallographic orientations of ZnO substrates under UHV conditions. The films are exposed to high pressure O<sub>2</sub> >1x10<sup>-3</sup> Torr, at temperatures above 300°C. Post exposure XPS is used to determine the conditions required for stable PdO formation. Angle resolved XPS is used to determine the location of the initial oxidation, either at the film surface or interface. The conditions for oxide formation on single crystal Pd(111) will be compared to the thin Pd-deposits on gold and for different ZnO-terminations. The formation of stable PdO is found to depend on the thickness of the initial Pd film. This study provides insight in the role of the support on the oxidation/reduction of Pd catalysts.

#### 8:40am SS-FrM2 Zinc Oxide Surface Chemistry, *J. Whitten*, University of Massachusetts Lowell

Zinc oxide is one of the most-studied and technologically relevant metal oxides and is particularly interesting because its nanoparticles are inherently photoluminescent. A variety of surface science techniques, including X-ray and ultraviolet photoelectron spectroscopies (XPS and UPS), have been used to investigate the adsorption of molecules on zinc oxide single crystal and nanoparticle surfaces. Adsorbates that have been studied include thiols, sulfur dioxide and nitrogen dioxide, and the effects of coadsorbates, such as water, have been evaluated. The effects of adsorption on the photoluminescence spectrum of ZnO have also been investigated. Applications of this research for electronic materials, heterogeneous catalysis, and dye-sensitized solar cells are discussed.

#### 9:00am SS-FrM3 Variations in the Orientation and Thermal Stability of the Carbonate Reaction Intermediate with the Surface Structure and Stoichiometry of Cerium Oxide Thin Films, *P.M. Albrecht, D.R. Mullins*, Oak Ridge National Laboratory

Carbonate, [CO<sub>3</sub>]<sup>2-</sup> is a stable intermediate in the water-gas shift reaction (CO + H<sub>2</sub>O → H<sub>2</sub> + CO<sub>2</sub>) over inverse CeO<sub>x</sub>/Au(111) catalysts, relevant to efficient H<sub>2</sub> production [1]. In addition, carbonate has recently been proposed as the high-temperature (600-700 K) intermediate in the dehydrogenation of methanol [2], and possibly in the complex reaction of acetaldehyde, on CeO<sub>2</sub>(100).

Here, we probe the formation and reaction of the carbonate species on CeO<sub>x</sub>(100) as a function of temperature and Ce oxidation state by adsorbing CO<sub>2</sub> at 180 K. There is a marked variation in the stability of the carbonate species with the crystallographic orientation of the ceria thin film. Temperature-programmed desorption (TPD) identifies CO<sub>2</sub> as the sole product, with desorption states at 230 K, 410 K, 510 K, and 655 K in the case of stoichiometric CeO<sub>2</sub>(100). On CeO<sub>2</sub>(111), carbonate desorbs entirely as CO<sub>2</sub> by 300 K [1, 3].

On CeO<sub>2</sub>(100), soft X-ray photoelectron spectroscopy (sXPS) confirms the persistence of carbonate up to 600 K. Near-edge X-ray absorption fine structure (NEXAFS) at the C *k*-edge shows a strong angular dependence that becomes more pronounced at higher temperature (lower coverage). The excitation of the π\* resonance at grazing incidence indicates that the carbonate is lying flat on CeO<sub>2</sub>(100).

For partially reduced CeO<sub>1.67</sub>(100), we observe: (1) A substantial decrease in low-temperature (< 250 K) desorption, (2) The appearance of an intense CO<sub>2</sub> desorption peak at higher temperature (765 K), and (3) The absence of well-defined peaks in the CO<sub>2</sub> desorption between 300 K and 600 K.

The integrated intensity of the [CO<sub>3</sub>]<sup>2-</sup> peak in the C 1s spectrum following CO<sub>2</sub> adsorption on CeO<sub>1.67</sub>(100) at 180 K is a factor of two greater than that for fully oxidized CeO<sub>2</sub>(100). On the reduced surface there is also no loss of this initial intensity upon heating to 300 K. At 700 K the carbonate coverage on the reduced surface is one-third of its starting value, whereas on the oxidized surface complete desorption (as CO<sub>2</sub>) has occurred.

Furthermore, resonant photoemission spectroscopy (RPES) indicates negligible re-oxidation of the CeO<sub>1.67</sub>(100) surface. In contrast, an RPES study of CO<sub>2</sub> on reduced CeO<sub>x</sub>(111) demonstrated partial re-oxidation at temperatures as low as 300 K [4].

Research sponsored by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, US Department of Energy.

[1] S. D. Senanayake et al., *J. Catal.* **271**, 392 (2010).

[2] P. M. Albrecht and D. R. Mullins, *Langmuir* **29**, 4559 (2013).

[3] S. D. Senanayake and D. R. Mullins, *J. Phys. Chem. C* **112**, 9744 (2008).

[4] T. Staudt et al., *J. Catal.* **275**, 181 (2010).

#### 9:20am SS-FrM4 Atomic Structure of the Anatase TiO<sub>2</sub>(001) Surface, *Y. Xia, K. Zhu*, Baylor University, *T.C. Kaspar*, Pacific Northwest National Laboratory, *B. Birmingham, K.T. Park, Z. Zhang*, Baylor University

Understand the atomic surface structure of well-defined anatase TiO<sub>2</sub>(001) surface is critical for deciphering site-specific thermal and photo-reaction mechanisms on anatase TiO<sub>2</sub> — the most reactive polymorph of TiO<sub>2</sub>. We have studied anatase TiO<sub>2</sub>(001) epitaxial thin films grown *ex-situ* by oxygen-plasma-assisted molecular beam epitaxy using UHV scanning tunneling microscopy (STM). Large (~30 nm) coexisting (4x1) and (1x4) reconstructed terraces are observed. The atomic corrugation on bright rows of the surface shows a strong bias voltage dependence and is not uniform. High resolution images resolve the atomic structure of the bright row. We propose a modified ad-molecule model for the anatase TiO<sub>2</sub> (001) surface structure.

#### 9:40am SS-FrM5 Study of Low Density Sites on Planar Silicon Dioxide Surfaces using Fluorescent Probes, *J.M. McCrate, J.G. Ekerdt*, University of Texas at Austin

Characterization of low density sites on planar oxide surfaces remains a challenging task. Such sites are believed to play an important role in catalysis and particle/film nucleation, although the inability to directly observe these sites limits our understanding of these processes. We have developed a technique that enables detection of low density sites on planar surfaces using fluorescent probe molecules. Derivatives of perylene, a high quantum yield fluorophore, with various functional groups are used to titrate surface sites in vacuum. The functional group is chosen to chemically bind to the desired site and *in situ* photoluminescence (PL) measurements are used to determine the density of sites and learn about their distribution. An estimated detection limit of < 10<sup>10</sup> sites / cm<sup>2</sup> is possible with this technique. We will discuss our work using fluorescent probes to study sites on the silica surface. In particular, results of our studies of strained siloxane with perylene-3-methanamine and oxygen vacancy defect (OVD) sites with 3-vinyl perylene will be presented.

#### 10:00am SS-FrM6 Functionalization of Vicinal Silicon Surfaces: Insight into Si Nanoparticle Reactivity, *W.J.I. DeBenedetti*, University of Texas at Dallas, *M.D. Halls*, Schrodinger Inc., *Y.J. Chabal*, University of Texas at Dallas

Semiconductor nanoparticle (NP) surface chemistry has long been recognized as central to the development and optimization of optoelectronic devices (based on NPs photoluminescence properties). Much attention has been directed to group II-VI quantum dots (QDs) for a variety of targeted applications, although their toxicity renders them incompatible with biological systems. Consequently, there is a renewed interest in nanostructured silicon that is more compatible with existing technology and more biologically friendly. Silicon NPs are capable of exhibiting high quantum yield emission and are considered environmentally adventurous compared to current Cd or Pb alternatives, but the origin of Si NP photoluminescence remains elusive. A significant advantage of using Si NPs is the ability to covalently modify their surface rather than employing datively bound ligands that can over time lead to aggregation, i.e. loss of optoelectronic properties. Though covalent surface modification of Si NPs has been realized, the mechanism of hydrosilylation at defect sites (steps) remains unknown, suggesting that work on model step surfaces could bring much needed insight.

Herein we report the functionalization of vicinal silicon (111) surfaces with both monohydride and dihydride step edges using a 9° off orientation in the (-1-12 & 11-2) directions, respectively. Two reactions are studied as a function of immersion time on both model surfaces: i) thermal hydrosilylation with a terminal alkene (known to be concerted on flat surfaces) and ii) nucleophilic addition using small molecule (methanol). It is found that the nucleophilic system reacts preferentially at the step edge

forming a bridge complex between the bridge and lower terrace hydrogen atoms (initial transition structure shown in Figure 1), while the alkene reacts with all terrace and step (mono- and di-hydride) sites. Such selectivity opens the door for nanopatterning and provides important insight into the behavior of Si NPs.

10:20am **SS-FrM7 Gallium Nitride Surface Preparation for ALD Deposition of Aluminum Oxide**, *A.J. Kerr, S. Gu, T. Kaufman-Osborn, E. Chagarov*, University of California, San Diego, *S. Madisetti*, University at Albany-SUNY, *P. Asbeck*, University of California, San Diego, *S. Oktyabrsky*, University at Albany-SUNY, *A.C. Kummel*, University of California, San Diego

Gallium nitride metal oxide semiconductor field-effect transistors (MOSFET) are promising candidates for high-speed and high-power circuits due to their voltage handling capability and high electron mobility. For these devices to function optimally, the oxide-semiconductor interface must have a low density of interfacial traps which can degrade performance and reliability. This study correlates the electrical properties and chemical bonding of deposited amorphous Al<sub>2</sub>O<sub>3</sub> on GaN(0001) prepared using ammonium sulfide solutions followed by in-situ atomic hydrogen cleaning.

A baseline CV measurement was made using simple TMA pre-dosing in the ALD system to reduce native oxide (Fig 1a). The ex-situ sulfide solution cleaning prior to cyclic atomic H and TMA pre-dosing resulted in improved C-V characteristics illustrated by decreased dispersion across the frequency spectrum. The greatest improvement in dispersion, however, was achieved when combining the ex-situ wet sulfur treatment with in-situ when atomic hydrogen plasma cleaning (Fig 1b.). To understand the role of the ex-situ wet sulfur treatment and in-situ atomic H cleaning, XPS, LEED, and SIMS were performed. Following wet sulfur treatment, in-situ XPS and LEED studies showed that heating to typical ALD temperatures (285°C) both removed the sulfur and produces a 1x1 LEED pattern consistent with less than a monolayer of disorder at the surface. SIM experiments upon the full oxide/GaN structures confirmed minimal sulfur at the buried oxide-semiconductor interface consistent with the main role of sulfur being to protect the surface against oxidation in air instead of providing a chemical passivation at the oxide/semiconductor interface. Angle resolved XPS studies of the ALD nucleation layers showed the primary role of the in-situ atomic hydrogen was to increase the initial growth rate of the gate oxide thereby increasing the ALD nucleation density consistent with previous reports demonstrating that atomic hydrogen completely removes native oxide. Density Functional Theory Molecular Dynamics (DFTMD) calculations (Fig. 2 and 3) were performed to compare the bonding of the amorphous Al<sub>2</sub>O<sub>3</sub> gate oxide to a bulk terminated GaN(0001) versus a GaN(0001) surface with a Ga adlayer. The bonding of the amorphous Al<sub>2</sub>O<sub>3</sub> gate oxide directly to the bulk terminated GaN(0001) was most consistent with the experimental results since this interface had bulk-like charge states for the interfacial atoms and a very low density of band gap states compared to even the clean GaN(0001) surface.

10:40am **SS-FrM8 Monolayer-induced Electronic Structure of Crystalline Semiconductor Surfaces**, *A.J. Makinen, C.-S. Kim, G.P. Kushto*, Naval Research Laboratory

Directly grafted organic monolayers on Si and Ge surfaces offer an interesting opportunity to explore aspects of surface passivation and control of electrical properties, namely, *molecular gating*, of semiconductor surfaces. We report our study of the interfacial electronic structures of *n*- and *p*-type of Si(111), Si(100) and Ge(111) surfaces that have been chemically modified with various organic monolayers. The investigated monolayers include octadecane, attached via hydrosilylation and hydrogermylation of 1-octadecene at Si and Ge surfaces, as well as para-substituted phenyl rings, attached by diazonium activation of hydrogenated Si and Ge surfaces. X-ray photoelectron spectroscopy of the modified Si and Ge surfaces, together with four-probe measurements of ultrathin (20-40 nm) silicon-on-insulator channels, functionalized with the monolayer structures, indicate that there is downward band bending, up to 200 meV, associated with assembling these organic monolayers on the semiconductor substrates. This band bending does not directly correlate with the dipole moment or electron withdrawing or donating character of the molecular moieties, pointing to the critical roles of the nature and quality of the self-assembled monolayer, and the intrinsic electronic structure of the semiconductor material in defining the interfacial electronic structure of the passivated Si and Ge surfaces.

11:00am **SS-FrM9 Probing Shallow Trapped Electrons in TiO<sub>2</sub> with UHV-IRRAS**, *H. Sezen, M. Buchholz, A. Nefedov, C. Natzeck, S. Heissler*, Karlsruhe Institute of Technology, Germany, *C. Di Valentin*, Università di Milano-Bicocca, Italy, *C. Wöll*, Karlsruhe Institute of Technology, Germany

Understanding photochemistry on oxide surfaces, a topic of pronounced importance in the context of solar fuel synthesis, includes tracking the path of the charge carriers photoexcited in the bulk to the surface where both, the electron and the hole, may induce chemical transformations in adsorbed molecular species. Shallow trap states which in the case of TiO<sub>2</sub> are known to store charge over extended periods of time (several hours) have a pronounced influence on this bulk-to-surface processes.[1-2] In this contribution we demonstrate that grazing-incidence IR-spectroscopy can be used to probe electrons localized in such states. Loading was carried out by either irradiation with UV-light or exposure to atomic hydrogen. For both, powders as well as a (110) oriented single crystal substrate of rutile titanium dioxide (r-TiO<sub>2</sub>), distinct IR absorption features were observed at around 940 and 970 cm<sup>-1</sup>. For the single crystal substrates, the IR absorption bands arising from an excitation of the trapped electrons into higher lying final states, are substantially sharper and, in addition, two new bands are resolved at 1205 cm<sup>-1</sup> and 1375 cm<sup>-1</sup>. On the basis of this new high-resolution data we propose that the trap state has to be described as a polaron state and that the final states correspond to hydrogenic states within the polaron potential.

[1] M. Xu, Y. Gao, E. M. Moreno, M. Kunst, M. Muhler, Y. Wang, H. Idriss, C. Wöll, *Phys. Rev. Lett.* **106**, 138302 (2011).

[2] D. A. Panayotov and J. T. Yates Jr, *Chem. Phys. Lett.* **436**, 204 (2007).

11:20am **SS-FrM10 Dependence on Experimental Ambient of Surface Photovoltage Transients in Nanostructured Oxide Surfaces and Interfaces**, *Y.M. Strzhemechny, P.R. Chapagain, A. Nemashkalo, S. Pant, E.S. Davis*, Texas Christian University

Kelvin probe-based surface photovoltage (SPV) measurements were employed to monitor super-bandgap transients in nanostructured oxide specimens placed in different environments – high vacuum, He gas, N<sub>2</sub> gas, etc. In general, contactless SPV transient experiments in semiconductors and insulators can provide information about surface/subsurface state densities and their cross sections, and these experiments sometimes reveal intricate illumination-mediated charge recombination mechanisms, especially in materials with a complex microstructure. The SPV time-domain response of the surface/subsurface states could also be significantly affected by the experimental environment, which was addressed in this work. Light-dark transient SPV were studied in several oxide systems with nanostructured morphologies at room temperature using a white light source: a nanoporous silicon permeated with Ni and Co nanoparticles, ZnO thin films on Si, as well as sol-gel samples on Si substrates containing titania/zirconia/silica mixed with noble metal nanoparticles. Some of the latter samples were also irradiated with a flux of Ti<sup>+</sup> ions. In most of these systems we observed nontrivial dynamics of charge redistribution in response to illumination changes and a strong dependence on the ambient. E.g., in the nanoporous Si samples, sharp ‘light on’/‘light off’ voltage spikes were detected in the He and N<sub>2</sub> gas environments, indicating several distinct charge exchange mechanisms occurring on dissimilar time scales. However, experiments on these specimens in high vacuum revealed a very different, albeit nontrivial response. On the other hand, for the multicomponent sol-gel thin films, a significant distinction was observed between the as-received and ion-irradiated samples. While for the as-received films the saturation curves in the N<sub>2</sub> and vacuum environments were similar, the irradiated samples yielded a much slower charge dynamics in vacuum compared to that in the N<sub>2</sub> atmosphere. We discuss possible mechanisms responsible for the observed SPV dynamics, related to the complex microstructure and its interaction with the environment.

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