

Wednesday Afternoon, October 20, 2010

Surface Science

Room: Santa Ana - Session SS-WeA

Chemisorption and Surface Reactions

Moderator: A. Utz, Tufts University

2:00pm **SS-WeA1 Characterization of the Chemical Signal Created by CO Oxidation on Pt/GaN Nanodiodes**, *J.R. Creighton, M.E. Coltrin, R.P. Pawlowski, K.C. Baucom*, Sandia National Laboratories

Previous results from Gabor Somorjai's group demonstrated the production of chemicurrent during catalytic reactions on Pt and Pd surfaces using a Schottky diode structure described as a "catalytic nanodiode" [1-2]. During the exothermic oxidation of CO, some fraction of the chemical energy may be dissipated by formation of hot electrons in the catalytic metal via electronic excitation. If the catalytic metal film is thin enough (nanometer scale) some of these hot electrons may be collected on the semiconductor side of the Schottky barrier in the form of a "chemicurrent". We have fabricated several versions of catalytic nanodiodes, and during CO oxidation we also detect a current that is unambiguously a result of the chemical reaction. We typically measure current densities up to 100 nA/mm² and reaction conversion efficiencies in the range of 10⁻⁵-10⁻³ electrons per CO₂ produced; results which are quantitatively similar to reports in more recent publications [3-4].

However, details of the electronic nature this chemical signal indicates that it is derived from a **voltage source**; not from a current source. In fact, the chemical signal is primarily, if not entirely, due to the thermoelectric voltage generated by changes in the **lateral** temperature gradient between the two electrical contacts in the nanodiode. We have used a 3D heat transfer model to simulate the time dependent temperature profile in the nanodiode during CO oxidation on Pt/GaN devices. This information, along with independent experimental measurements of the Seebeck coefficient allows us to quantitatively simulate the thermoelectric voltage signal generated during a typical experiment involving time-dependent CO oxidation. Our results indicate that the nanodiode is simply operating as a **thermal detector** via a thermoelectric voltage. Unfortunately we have not yet found evidence supporting true "chemicurrent" formation during CO oxidation on Pt/GaN nanodiodes.

References:

- [1] Z.J. Xiao and G.A. Somorjai, *J. Phys. Chem. B* 109 (2005) 22530.
- [2] J. Xiaozhong, A. Zuppero, J.M. Gidwani, and G.A. Somorjai, *J. Amer. Chem. Soc.* 127 (2005) 5792.
- [3] J.Y. Park, J. R. Renzas, B.B. Hsu, and G.A. Somorjai, *J. Phys. Chem. C*, 111 (2007) 15331
- [4] J.Y. Park, J. R. Renzas, A.M. Contreras, and G.A. Somorjai, *Topics in Catalysis*, 46 (2007) 217

2:20pm **SS-WeA2 Structural Investigation of Methylthiolate/Au (111) Interface: A Photoemission Core Level Shift Study**, *A. Chaudhuri*, University of California, Irvine

Self assembled monolayers have been the subject of considerable interest for the last two decades. The high order, dense and stable structures, and bio compatible nature of these systems make them interesting for a wide range of technological application in industry. The thiolate /Au(111) interface is regarded as one of the classical examples of self assembled monolayer systems and is ideal for study in laboratories, due to the robust nature of the surface.

Despite of a number of studies, the adsorption sites of the thiolate and, hence, the structure of this interface is a long standing controversial issue. The conflict between theoretical calculations and the experimental observations for thiol-Au system has been fuelled by contradictory models to determine the adsorption site based on different experimental techniques. These models are different from each other and fail to depict a mechanism for a complete structure formation. In this present work, we have investigated the local structure of methylthiolate in the ordered Au(111) - ($\sqrt{3}\times\sqrt{3}$)R30° phase using core-level- shifts measurements of the surface and bulk components of Au 4f_{7/2} photoelectron binding energy.

2:40pm **SS-WeA3 Mechanistic Study of Photochemical Grafting of Alkenes to Group IV Semiconductors**, *X. Wang, R.J. Hamers, R. Ruther*, University of Wisconsin-Madison

The grafting of organic molecules on semiconductor surfaces initiated by UV light has become an efficient means to tailor the chemical and physical properties of surfaces of materials, enabling their integration with various

applications of the devices. The mechanism of photochemical grafting of alkenes to group IV semiconductors (diamond, silicon, germanium, etc) has remained poorly understood. We have demonstrated that a previously unrecognized process—photoelectron emission from semiconductors to reactant liquid—is a nearly universal mechanism for initiating grafting of alkenes to surfaces and is broadly applicable to a wide range of semiconductors.

The charge transfer processes that occur during the photochemical grafting to diamond surfaces were investigated by spectrally resolved photoelectron yield experiments. X-ray and ultraviolet photoelectron spectroscopy measurements (XPS, UPS) establish a clear correlation between the photoelectron yield, the grafting efficiency at different wavelengths, and the valence electronic structure of the substrate and of the reactant molecule.

While our initial work focused on detailed studies on diamond, more recently we have shown that this mechanism is also responsible for initiating UV-induced grafting onto other semiconductors, most notably both silicon and germanium. By intentionally reducing the bulk carrier lifetime in Si (by doping with Au) and comparing the grafting efficiency, we showed that the rate of UV-induced grafting is independent of the bulk carrier lifetime. This observation is important as it allows us to immediately rule out the bulk exciton mechanism as the primary pathway. Our results also showed that the rate of grafting was directly connected to the electron affinity of the reactant molecules. These results are important because they show that photoemission can also dominate as an initiation process with smaller bandgap semiconductors, such as silicon and germanium, where photoemission and exciton processes can both take place. We have hypothesized that the reason why the photoemission can be dominant even on silicon is that photoemission is an irreversible process, while in an exciton process the concentration of holes is reduced by recombination processes. Our studies provide new insights into the nature of photochemical functionalization on the surfaces of semiconductors and a fundamental understanding of the mechanism will facilitate the design and synthesis of well defined functional interfaces.

3:00pm **SS-WeA4 Reaction of Diisocyanates at the Ge(100)-2 × 1 Surface**, *K.T. Wong, S.N. Chopra, S.F. Bent*, Stanford University

Interest in organic functionalization of semiconductors has increased in recent years, as it offers the ability to mate existing knowledge of microelectronics fabrication with the tailorability of organic molecules to precisely control interfacial properties. Such control is necessary for today's microelectronics with continually decreasing feature sizes. In particular, this study focuses on organic functionalization of the germanium surface; germanium is a group IV semiconductor, like silicon, which may be used in devices for its favorable electronic properties. Here, we study the adsorption of two diisocyanate molecules on the Ge surface: 1,3-phenylene diisocyanate, in which the isocyanate functional groups are connected by a relatively stiff phenylene ring, and 1,4-diisocyanatobutane, in which they are connected by a more flexible alkyl chain. Using multiple internal reflection Fourier transform infrared spectroscopy in ultra high vacuum, we show that both molecules bind to the Ge(100)-2×1 surface primarily by a [2+2] cycloaddition reaction across the C=N bond of one isocyanate functional group. This result is similar to previous results for other isocyanate-containing molecules reacted with the Ge(100)-2×1 surface. X-ray photoelectron spectroscopy results agree with the [2+2] cycloaddition assignment and provide evidence that some isocyanate functional groups interact with the surface via a dative bond through an oxygen lone pair. We propose that this is likely the result of some adsorbates forming an additional interaction with the surface through the second isocyanate functional group. Density functional theory calculations demonstrate the feasibility of such products. The relatively weak binding of a second functional group by dative bonding may make these molecules ideal candidates for studying displacement by subsequent exposure to a second precursor. It may be possible to displace the dative-bonded isocyanate functional group, thereby creating additional free isocyanate groups on the surface.

4:00pm **SS-WeA7 Multiple Time and Length Scales in Nanocatalysts Probed in a Single Synchrotron Experiment: The Combined use of XAFS, XRD, DAFS and IR**, *A.I. Frenkel*, Yeshiva University **INVITED** X-ray absorption fine structure (XAFS) and x-ray diffraction (XRD) techniques give complementary information about the structure of catalytic materials. XRD is effective in crystalline materials that possess medium to long range order (bulk catalysts, substrates and templates) while XAFS provides short range structural details in disordered, amorphous and/or low-dimensional materials. In addition, XAFS gives information about the electronic properties of the catalysts. These two methods have been developed and advanced *independently* from each other at synchrotron

sources in the US and abroad. To analyze catalysts *in situ*, in particularly *in operando* (under their operating conditions), a new approach is needed, namely, the simultaneous collection of the XRD and XAFS data in real time as the reaction progresses, together with the online product analysis. Diffraction Anomalous Fine Structure (DAFS) is a structure-sensitive technique that allows to deconvolute multiple phases of the same element (e.g., metal nanoparticles and metal oxide) that can coexist in the sample. Application of quick scanning monochromator mode to XAFS measurement (called QEXAFS) allows to study kinetics of structural transformations within the reactants, catalysts and the reaction products. Such combinations allow to measure the time-dependent changes in the *actual* structure (in the short, medium and long range order), electronic properties and chemical activity of catalysts synchronously.

The first in US dedicated instrument for such combined measurements was built at the beamlines X18A and X18B of the National Synchrotron Light Source at Brookhaven National Laboratory. The current setup includes transmission and fluorescence XAFS detectors, QEXAFS monochromator enabling 10ms time EXAFS scan time, 2D area detector for XRD, residual gas analyzer and the automated gas mixing system. The upgrades currently under way include the addition of Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) instruments developed jointly by members of Synchrotron Catalysis Consortium at BNL and Harrick Scientific.

I will present several applications of the combined use of these instruments for catalysis research, including the studies of kinetics of reduction and oxidation of Cu-ceria catalysts, the investigation of the mechanism of reduction of CuFe_2O_4 with CO, and others.

4:40pm SS-WeA9 The Interaction of Oxygen with Single Crystal Stepped Copper Surfaces: a XPS and STM Study, E. Broitman, Carnegie Mellon University, V.V. Pushkarev, Lawrence Berkeley National Laboratory, B.S. Holsclaw, Carnegie Mellon University, T.J. Lawton, A.E. Baber, E.C.H. Sykes, Tufts University, A.J. Gellman, Carnegie Mellon University

Fundamental knowledge of metal oxidation processes is an important problem for the understanding of corrosion. In particular, the oxygen reaction with copper surfaces is considered to be a model system and has consequently been extensively studied. However, to our knowledge, most of the studies have been carried out in individual samples of single orientations. In this work, the influence of steps on the oxidation of copper surfaces is studied by the use of a spherically-shaped sample with a (111) plane in its center. This sample allows the possibility to study the orientation dependence continuously up to a deviation of 10° from the (111) plane.

The copper crystal was cleaned in a UHV preparation chamber with a base pressure $< 1 \times 10^{-10}$ Torr using several cycles of sputter cleaning with Ar^+ ions of 1 KeV energy and annealing up to 600°C . The sample, kept at room temperature, was subsequently exposed to oxygen using a leak valve with dosing values in the range 100 to 1000 Langmuir. Two-dimensional surface imaging chemical analysis was carried out at room temperature using a Theta Probe monochromated Al K_{α} x-ray photoelectron spectroscopy (XPS) system (Thermo Scientific) in snapshot mode with a $100 \mu\text{m}$ spot size. Data processing was performed using the software Advantage provided with the instrument. Scanning Tunneling Microscopy (STM) was also done at room temperature using a commercially available STM Variable Temperature system (Omicron).

XPS images have shown that the oxygen content in the surface increases in the areas with higher step density. STM images revealed a complex oxidation mechanism. Adsorption of oxygen leads to the formation of a surface oxide by preferential incorporation of Cu atoms from step edges. It was observed at higher dosing that the descending step edge to a large terrace results to be more faceted and jagged than a descending step edge of a smaller terrace. It can be assumed that oxygen landing on the terrace diffuses to the descending step edge and oxidizes it. In this way, larger terraces above a step edge would have more oxygen diffusing to the descending step edge, producing more faceting than in the descending steps of the smaller terraces.

5:00pm SS-WeA10 Cu(100) Oxidation: Potential Copper-Releasing Pathways for $c(2 \times 2)$ to Missing-Row Reconstruction Transition, M. Lee, A.J.H. McGaughey, Carnegie Mellon University, J.C. Yang, University of Pittsburgh

Previous experimental and theoretical results show that the $(2\sqrt{2} \times \sqrt{2})R45^\circ$ missing-row reconstruction is a stable intermediate state during the early stages of Cu(100) oxidation. When the oxygen coverage on a Cu(100) surface reaches 0.5 monolayers [the $c(2 \times 2)$ phase], the surface structure transforms into the missing-row reconstruction by the release of every fourth row of copper atoms from the top copper layer. The released copper atoms are assumed to then diffuse away. The specific mechanisms and

energetics of this transition are not yet fully understood. To investigate this transition, we use density functional theory calculations to predict potential copper-releasing pathways and their energy barriers using the climbing image nudged elastic band method. In the $p(2\sqrt{2} \times \sqrt{2})$ unit-cell, there are two potential copper releasing pathways. For each pathway, two energy barriers are predicted because there is an intermediate state between the $c(2 \times 2)$ phase and the missing-row reconstruction. The energy barriers are 1.61 eV and 1.04 eV for the first pathway and 2.19 eV and 0.38 eV for the second pathway. To assess system size effects and alternative pathways, we also investigate the $p(2\sqrt{2} \times 2\sqrt{2})$ and $p(4 \times 4)$ unit-cells. In applying the copper releasing pathways analyzed for the $p(2\sqrt{2} \times \sqrt{2})$ unit-cell to the larger unit-cells, there will be multiple ways to arrive at the final state. For example, in the $p(2\sqrt{2} \times 2\sqrt{2})$ unit-cell, two copper atoms should be released to form a complete missing-row. There are two ways for the missing-row formation: moving the copper atoms one by one or moving two copper atoms together. We expect that the copper releasing pathways and energy barriers will vary with the nature of the releasing copper movements.

5:20pm SS-WeA11 Formation, Characterization and Reactivity of Adsorbed Oxygen on BaO/Pt(111), K. Mudiyansele, Pacific Northwest National Laboratory, C.-W. Yi, Sungshin Women's University, Republic of Korea, J. Szanyi, Pacific Northwest National Laboratory

The formation of O_{ad} species and their reactivities in CO oxidation on BaO/Pt(111) were studied with temperature programmed desorption (TPD), infrared reflection absorption (IRA) and X-ray photoelectron (XP) spectroscopies. Two BaO/Pt(111) model systems with different BaO coverages were prepared and studied. The Pt(111) surface in both of these systems was not completely covered with BaO. On the system with lower BaO coverage ($\sim 50\%$ of the Pt(111) surface was free of BaO), two different O_{ad} species form following the adsorption of O_2 at 300 K; O adsorbed on clean Pt(111) sites and at the Pt-BaO interface. On the system with higher BaO coverage ($\sim 70\%$ of the Pt(111) surface is covered by BaO) two types of O_{ad} are seen at the Pt/BaO interface. The desorption of oxygen from the BaO-free portion of the Pt(111) surface gives an O_2 desorption peak with a maximum desorption rate at ~ 690 K. Recombinative desorption of interfacial O_{ad} gives two explosive-desorption features at ~ 760 and ~ 790 K in the TPD spectrum. The reactivities of these adsorbed O species with CO to form CO_2 follow their order of desorption; i.e., the O_{ad} associated with the clean Pt(111) surface and desorbs at 690 K reacts first with CO, followed by the O_{ad} species at the BaO/Pt(111) interface (first the one that desorbs at ~ 760 K and finally the one that is bound the most strongly to the interface, and desorbs at ~ 790 K).

5:40pm SS-WeA12 Molecular Vibrations at Surfaces by First-Principles Molecular Dynamics: Hydrogen-Bonded Networks of Amino Acids on Copper, A. Ievins, S.J. Jenkins, University of Cambridge, UK

We present first-principles molecular dynamics simulations, obtained at the density functional level of theory, for molecular vibrations of amino acids on copper surfaces. Specifically, we have studied the hydrogen-bonded networks formed by glycine and alanine on the $\text{Cu}\{110\}$ and $\text{Cu}\{311\}$ surfaces. Fourier transformation of the autocorrelation function in each case leads to frequency spectra that may be compared with data from infra-red absorption experiments, where available. Moreover, by separately Fourier transforming key structural parameters such as individual bond lengths or bond angles, it is possible to make confident band assignments that aid in the interpretation of experiment. By tracking the motion of atoms over time, it is also possible to extract mean atomic positions, and realistic thermal ellipsoids, which may in turn be of use in understanding results from diffraction experiments and/or scanning tunneling microscopy.

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