

# Thursday Morning, November 12, 2009

## In Situ Microscopy and Spectroscopy: Interfacial and Nanoscale Science Topical Conference

Room: C4 - Session IS+SS-ThM

### In-Situ Spectroscopy - Interfacial Science & Catalysis

Moderator: D.R. Baer, Pacific Northwest National Laboratory

8:00am **IS+SS-ThM1 Reduction of Cationic Sn in SnO<sub>x</sub>/PtSn Alloy Surfaces**, *G. Liu*, Lehigh University, *H. Bluhm*, Lawrence Berkeley National Laboratory, *B. Koel*, Lehigh University

Understanding mechanisms of catalyst selectivity requires improved knowledge of oxidation and reduction reactions that occur at the metal/metal oxide interface. We describe studies that probe the thermal stability and reducibility of cationic Sn at SnO<sub>x</sub>/PtSn alloy interfaces for several different and well-defined surface phases of SnO<sub>x</sub> that can be formed depending on the temperature. Our investigations covered a wide range of conditions, from vacuum to the chemical changes during exposures to H<sub>2</sub> at pressures up to 5 Torr by using in-situ high pressure photoelectron spectroscopy (HP-PES). We find enormous differences in the reducibility of cationic Sn species showing that local surface structure and composition plays an key role in governing these reactions. These studies help to define the overall chemical reactivity of SnO<sub>x</sub> species at these interfaces, and in particular, clarify the role of reduced and cationic Sn sites in selective hydrogenation of crotonaldehyde.

8:20am **IS+SS-ThM2 In-situ Study of the Oxidation of Pt(110)**, *M. Grass*, *D. Butcher*, *F. Aksoy*, *H. Bluhm*, *G.A. Somorjai*, *Z. Hussein*, Lawrence Berkeley National Laboratory, *B.S. Mun*, Hanyang University, Korea, *Z. Liu*, Lawrence Berkeley National Laboratory

The formation of oxides on transition metal surfaces has been actively studied because of its importance in understanding heterogeneous catalytic reactions on metal surfaces. In particular, the study of surface oxides on Pt(110) has received much attention. Oxidation reactions over Pt are both industrially significant and fundamentally intriguing. In particular, there has recently been much debate over the surface structure and reaction mechanism of CO oxidation at high O<sub>2</sub>/CO ratios on Pt(110).

In this study, we used both ambient pressure x-ray photoelectron spectroscopy (AP-XPS) and high pressure scanning tunneling microscopy (HP-STM) to investigate oxidation of Pt(110) as a function of O<sub>2</sub> pressure, temperature and gas composition (CO, O<sub>2</sub>). AP-XPS results demonstrate that two different surface oxygen species form on Pt(110) surface above 500 mTorr O<sub>2</sub>: chemisorbed oxygen and an island structured species that extends at least two Pt layers deep. HP-STM images under the same conditions confirm the formation of these oxide islands. We present here the pressure and temperature dependence of both oxygen species as well as kinetic measurements of the reaction CO<sub>ad</sub> + O<sub>ad</sub> → CO<sub>2</sub> for each of the adsorbed oxygen species.

The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Light Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

8:40am **IS+SS-ThM3 Composition and Chemistry of the Liquid/Vapor Interface by In-Situ X-ray Photoelectron Spectroscopy**, *J.C. Hemminger*, University of California, Irvine **INVITED**

We use synchrotron based x-ray photoelectron spectroscopy (XPS) experiments to study the composition and chemistry at the liquid/vapor interface of aqueous solutions. These experiments are motivated by an interest in the fundamental behavior of aqueous interfaces as well as applications to aqueous aerosols in the atmosphere. We take advantage of the variable energy characteristic of synchrotron radiation to carry out XPS experiments as a function of experimental probing depth, thereby generating a depth profile of the liquid/vapor interface. Recent experiments in which we have studied the composition of aqueous salt solutions in the presence of organic surfactants will be described. In addition, studies of acid/base equilibria at the liquid/vapor interface will be described. Our depth profile experiments show that the acid/base equilibrium at the solution surface is modified by the differences in bulk solubility of the acid and base involved in the equilibrium. Two different experimental approaches have been used: an ambient pressure end station at the Advanced light source is equipped with a differentially pumped electron

energy analyzer allowing studies with the sample chamber at pressures of a few torr. This system has been used to study saturated aqueous solutions of alkali halide salts. A liquid/jet endstation at the BESSY synchrotron has allowed us to study the surface segregation of molecular ions such as nitrate in aqueous solutions as a function of solution concentrations.

9:20am **IS+SS-ThM5 Oxidation Studies of Gold by in Situ High-Pressure X-ray Photoelectron Spectroscopy**, *F. Borondics*, *P. Jiang*, Lawrence Berkeley National Laboratory, *S. Porsgaard*, Lawrence Berkeley National Laboratory & iNANO University of Aarhus, Denmark, *M. Köber*, *A. Caballero*, *H. Bluhm*, *M. Salmeron*, Lawrence Berkeley National Laboratory

The high catalytic activity of nanometer size gold particles in various chemical reactions has been intensively investigated in the recent years. However the origin of the exceptional catalytic properties of Au is still strongly debated in many cases ranging from the mobilization of gold under catalytic conditions through the oxidation state of the active Au species during the reaction.

In this study we focus on the interaction of oxygen with Au that has been proposed to play an important role in the mechanism of oxidation reactions. Using in situ high-pressure X-ray photoelectron spectroscopy (HP-XPS) and in situ scanning electron microscopy we studied the different model systems, such as bulk gold, evaporated sub-monolayer and different size nanoparticle samples using single crystalline TiO<sub>2</sub> (110) as substrate.

Our results show that gold oxidation can be induced under certain conditions, such as high intensity X-rays or reactive ozone atmosphere. The existence of gold oxide has been mentioned in the literature, but our systematic studies provide a better understanding of the formation and stability of this compound, which is not only a chemical curiosity being the oxide of the noblest metal, but can be very important in designing more efficient catalysts. In addition, we would like to draw the attention of the community to a number of artifacts that can easily lead to misinterpretation of experimental data.

The implications of our results should be considered in the field of catalysis, nano- and surface science as well as in situ high-energy spectroscopies.

9:40am **IS+SS-ThM6 Anchoring of N3 Dye Molecule on TiO<sub>2</sub>(110) Surface and its Influence on Energy Level Alignments**, *P. Nachimuthu*, Pacific Northwest National Laboratory, *Z.Q. Yu*, Nanjing Normal University, China, *Z. Zhu*, *K.M. Beck*, *S. Thevuthasan*, *M.A. Henderson*, Pacific Northwest National Laboratory

In dye-sensitized solar cells, the electronic coupling between the dye-sensitizer and TiO<sub>2</sub> determines the alignment of energy levels and the electron transfer dynamics. This electronic coupling is strongly modified by the way in which the dye molecules are adsorbed and anchored to TiO<sub>2</sub> surface, its relative orientations and geometrical structures. The present study is an attempt to understand how the dye molecules are bound to TiO<sub>2</sub> single crystal surface and their influence on the energy level alignments and electron transfer dynamics. Controlled adsorption of dye molecules (bis(4,4'-dicarboxy-2,2'-bipyridine)-bis(isothiocyanato)ruthenium(II) is known as N3) onto TiO<sub>2</sub> surface has been carried out to obtain desired anchoring and orientations by varying the concentration, hydrophobic substituents on dye and defect concentrations (in TiO<sub>2</sub>). ToF-SIMS and PEEM mapping techniques were used to understand the distribution of dye molecules on TiO<sub>2</sub> surface. The XPS and UPS measurements were carried out to determine the structural and electronic properties including the stoichiometry of dye molecules on TiO<sub>2</sub> surface, the relative energy levels and band offsets in the absence and presence of UV light. The XPS results show that the atomic ratios of S to Ru and N to S are ~1 and ~5, respectively, which correspond to a non-stoichiometric composition of N3 molecule on TiO<sub>2</sub> surface. The theoretical atomic ratios of S to Ru and N to S in N3 molecules are 2 and 3, respectively. This suggests that an isothiocyanide group from N3 molecule is lost from the surface of TiO<sub>2</sub>. The XPS from multilayers of N3 molecules on Si surface however show stoichiometric composition.

10:40am **IS+SS-ThM9 Scanning Transmission X-ray Microscopy of Inorganic and Organic Nanoparticles in the Environment**, *S.C.B. Myneni*, Princeton University **INVITED**

Inorganic and organic nanoparticles are common in the environment, and play an important role in the biogeochemical reactions occurring in the natural systems. However, their chemistry and behavior are poorly understood. Using STXM, researchers can examine the chemistry and mineralogy of these particles, and the functional group chemistry of associated organic molecules. While XANES spectral features are used routinely to identify the oxidation states of elements in minerals

successfully, fine variations in spectral features of minerals can be used in the identification of minerals and the crystallinity of precipitates/nanoparticles. The XANES spectra are also sensitive to different functional groups and their protonation (or deprotonation) and metal complexation; unique features in XANES spectra can also be used in mapping the distribution and relative concentrations of organic molecules and their complexes at a resolution better than 25 nm in environmental samples. In the last 4-5 years, we made significant progress in the understanding of the mineralogy and chemistry of important environmental nanoparticles and biominerals because of the development of STXM capabilities. A summary of applications of STXM in studying environmental nanoparticles, and highlights of some of these recent findings will be discussed.

11:20am **IS+SS-ThM11 In-situ Characterization of Arsenic on Model Iron Oxide Surfaces**, *S. Kaya, F. Mbuga*, SLAC National Accelerator Lab, *T. Kendelewicz*, Stanford University, *J. Newberg, H. Bluhm*, Lawrence Berkeley National Lab, *H. Ogasawara*, SLAC National Accelerator Lab, *G.E. Brown*, Stanford University, *A. Nilsson*, SLAC National Accelerator Lab

Natural contamination of groundwater by arsenic has become an important water quality problem in many parts of the world [1]. Arsenite [As(III)] and arsenate [As(V)] are highly toxic inorganic arsenic species that represent a potential threat to the environment and human health. Iron oxides play a significant role in controlling dissolved As concentration and limit the mobility and availability of As(III) and As(V). Arsenic adsorption mechanisms involve exchange of the As species for surface water and surface OH groups therefore in-situ characterizations of iron oxide surfaces in the presence of water are crucial.

We have studied chemical nature of As on Fe<sub>3</sub>O<sub>4</sub>(111) and Fe<sub>3</sub>O<sub>4</sub>(111)/Fe(OH)<sub>x</sub> thin films in the presence of water (P<0.5 Torr) using Ambient Pressure Photoemission Spectroscopy (APPES) at Advanced Light Source (ALS) [2]. Hydroxylation of pristine Fe<sub>3</sub>O<sub>4</sub>(111) surface commences at low relative humidity (RH) values and is followed by adsorption of molecular water with increasing RH. In 0.5 Torr water H<sub>2</sub>O:OH ratio at room temperature is about one and all acidic sites are fully hydroxylated. As 3d spectra taken in presence of 0.5 Torr water suggests that oxidation state of arsenic depends on degree of hydroxylation of iron oxide surfaces studied. In addition to the hydroxylation process, increasing RH leads to oxidation of arsenic from As(III) to As (V). Fe<sup>2+</sup> surface sites plays an important role in the oxidation states of arsenic and the reasons of which will be discussed based on the changes in formal charges during hydration-dehydration processes.

[1] R. Nickson, et. al., *Nature*, 395 338 (1998).

[2] H. Bluhm et al., *MRS Bulletin*, 34 1022 (2007).

11:40am **IS+SS-ThM12 Kinetic Studies of the Dissociation of Molecular Oxygen on Pt(111)**, *H. Ogasawara, L.-Å. Näslund, D.J. Miller, T. Anniyev, A. Nilsson*, Stanford Synchrotron Radiation Lightsource

Thermally programmed X-ray photoelectron spectroscopy was used to study the dissociation of molecular oxygen on Pt(111) under ultrahigh vacuum conditions. Sub-monolayer coverages of molecular oxygen were dosed onto a clean crystal of Pt(111) at 60 K, a temperature well below the dissociation onset of roughly 95 K. Kinetic analysis of the XPS data indicate that they are consistent with a barrier to O<sub>2</sub> dissociation that is less than 0.4 eV. This result is in striking contrast to the most recent theoretical studies with density functional theory, which all indicate barriers in excess of 0.5 eV (0.5 - 0.9 eV). On the basis of this low observed barrier, we speculate that the direct dissociation of molecular oxygen could be a viable alternative to the associative and peroxide pathways that are presently assumed to be operative in the oxygen reduction reaction.

# Thursday Afternoon, November 12, 2009

## In Situ Microscopy and Spectroscopy: Interfacial and Nanoscale Science Topical Conference Room: C4 - Session IS+AS-ThA

### In-Situ Microscopy and Spectroscopy: Surface Reactions Moderator: P. Nachimuthu, Pacific Northwest National Laboratory

2:00pm **IS+AS-ThA1 Interface Science in Nanoparticles: An Electronic Structure View of Photon-in/Photon-out Soft-X-Ray Spectroscopy.** *J.-H. Guo*, Lawrence Berkeley National Laboratory  
Solar energy can be converted to electricity and chemical fuels for energy use and storage. However, the cost and conversion efficiency have been the biggest challenge for potential use of solar energy. There are the emerging technologies of using semiconductors for light harvesting assemblies; and charge transfer processes to solar cells. It could provide a significant contribution to our electrical and chemical resources if efficient and inexpensive systems utilizing readily available materials could be devised for the conversion process.

This presentation will shed some light on synchrotron radiation based soft-x-ray spectroscopy study of nanostructured materials. Soft-x-ray absorption probes the local *unoccupied* electronic structure (conduction band); soft-x-ray emission probes the *occupied* electronic structure (valence band); and the addition of resonant inelastic soft-x-ray scattering (Raman spectroscopy with soft x-rays) can tell the energy levels that reflect the chemical and physical properties of semiconductors. The experimental studies suggest that in-situ photon-in/photon-out soft-x-ray spectroscopy becomes an emerging tool for investigating the surface and interface science.

(1) The examples show quantum size effects on the exciton and band-gap energies of semiconductor nanocrystals (Hematite nanoarrays). Such finding strongly suggests that such designed nanomaterials could meet the bandgap requirement for the photocatalytic oxidation of water without an applied bias.

(2) The storage of hydrogen in a both safe and compact manner is of great importance for, for example, hydrogen powered vehicles. We have explored in-situ photon-in/photon-out soft-X-ray spectroscopy to study the molecular adsorption of H<sub>2</sub> on SWNTs under ambient pressures. The spectral changes with the increasing gas pressures provide the strong evidences for the tube-wall structure deformation and possibly a fraction of charge transfer due to the gas collision.

2:20pm **IS+AS-ThA2 In Situ GIXAFS and HERFD-XAS Studies of Pt-modified Rh(111) and Rh(221) Electrodes.** *D. Friebe, D.J. Miller, H. Ogasawara, T. Annyev, C.P. O'Grady, U. Bergmann, J. Bargar, A. Nilsson, Stanford Synchrotron Radiation Lightsource, K.T. Wikfeldt, L.G.M. Pettersson*, Stockholm University, Sweden

The oxygen reduction reaction at Pt electrodes has a high overpotential which drastically reduces the efficiency of fuel cells. The origin of the overpotential has been seen in the formation of stable Pt-O species at high potentials. Aiming at an unambiguous characterization of such Pt-O species, we use in situ grazing incidence x-ray absorption spectroscopy at the Pt L<sub>3</sub> edge to study the geometric and electronic structure of ultrathin Pt layers on Rh(111) and Rh(221) substrates as a function of the electrochemical potential. The use of Pt monolayers on a foreign metal substrate makes the bulk-penetrating hard x-ray probe surface sensitive and, furthermore, can be used for a variety of substrates to elucidate the influence of metal-metal interactions and interfacial strain on the catalytic activity of the Pt layer. The stepped Rh(221) surface serves as a well defined model substrate to study the influence of defects which are also expected to occur in nanoparticle catalysts.

We present our results from Pt L<sub>3</sub>-edge grazing incidence x-ray absorption fine structure (GIXAFS) and high energy resolution fluorescence detection (HERFD) XAS measurements of an ultrathin Pt layer on Rh(111) in 0.01 M HClO<sub>4</sub> solution. The Pt layer was produced by UHV evaporation. In the HERFD-XAS experiment, we used a multi-crystal analyzer to reduce the core hole lifetime broadening. The high resolution spectra reveal additional spectral features of the near-edge region which can be theoretically modeled using the FEFF8 code and thus allow us to build an accurate structure model of the Pt/electrolyte interface.

2:40pm **IS+AS-ThA3 Chemical Imaging of Catalytic Solids at the Micron- and Nanoscale.** *B.M. Weckhuysen, E. de Smit*, Utrecht University, the Netherlands **INVITED**

Most characterization studies of catalytic solids focus on ensemble-averaged measurements, assuming that catalytic solids are spatially homogeneous materials when placed in a reactor. Structure-performance relationships can then be obtained by relating activity and selectivity with a multitude of spectroscopic signatures. However, these signatures are not necessarily identical across e.g. a catalyst grain or fixed bed reactor. Detailed knowledge on these spatial heterogeneities is required to better understand reaction and deactivation mechanism. This keynote lecture discusses the potential of spectroscopic methods for chemical imaging spatial heterogeneities within catalytic solids at the micron- and nanoscale. Special emphasis will be on the use of in situ Scanning Transmission X-ray microscopy (STXM), UV-Vis microscopy, synchrotron IR microscopy, Coherent Anti-Stokes Raman Scattering (CARS) microscopy and (confocal) fluorescence microscopy. Two showcases will be discussed, namely Fe-based Fischer-Tropsch Synthesis (FTS) and H-ZSM-5 zeolites, catalyzing the oligomerisation of styrene and methanol to hydrocarbons. For the latter showcase, large coffin-shaped H-ZSM-5 crystals have been studied.

3:40pm **IS+AS-ThA6 Using Synchrotron Based in situ X-ray Techniques and TEM to Study Electrode Materials for Lithium Batteries.** *X.Q. Yang*, Brookhaven National Laboratory **INVITED**

Recently, we have developed techniques using the combination of a high intensity synchrotron x-ray beam and fast detectors (image plate or position sensitive detectors) to do in-situ X-ray diffraction (XRD) during charge-discharge cycling and time resolved X-ray diffraction during the thermal decomposition of charged cathode materials. We have also developed synchrotron based in-situ X-ray absorption (XAS) techniques to study the changes of oxidation states and coordination of the transition metal elements during cycling. The in-situ and ex-situ soft x-ray absorption spectroscopy techniques we have developed allow us to distinguish the structural differences between the surface and bulk of electrodes using both electron yield (EY) and fluorescence yield (FY) detectors simultaneously. In this presentation, we will report our studies on the structural changes of various cathode materials such as layered LiMO<sub>2</sub> (M=Co, Mn, Ni) and olivine structured LiMPO<sub>4</sub> (M=Fe, Mn, Co, Ni) with and without surface coating, during charge-discharge cycling as well as during thermal decompositions. The results of these studies provide very important information for synthesizing new cathode materials with improved properties. Preliminary results of studies using in-situ transmission electron microscopy and high-resolution analyses will also be reported. **ACKNOWLEDGMENT** This work done at Brookhaven National Lab. was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies of the U.S. DOE under Contract No. DE-AC02-98CH10886

4:20pm **IS+AS-ThA8 Direct Observation of Interfacial Layer Formation in Li-Ion Battery using In-Situ TEM and EELS.** *C.M. Wang, W. Xu, L. Saraf, B. Arey, J. Liu, Z. Yang, J.G. Zhang, S. Thevuthasan, D.R. Baer*, Pacific Northwest National Laboratory

One of the fundamental challenges facing the Li-ion battery development is the understanding of the fading mechanism of the active electrode materials during the repeated charging and discharging. In-situ methods based on x-rays have provided some information regarding the structural evolution of the electrode materials during the operation of a battery. However, in-situ work using x-ray only gives the average results, yielding no spatial resolution. Furthermore, it has been generally realized that the microstructural evolutions both at the interface between the electrolyte and the electrode and within the electrode (active materials) due to Li migration play a vital role on the performance as well as the overall life-cycle of the battery. In-situ transmission electron microscopy (TEM) and spectroscopy will be ideal tools for probing the structural evolution of the electrode materials during battery operation. However, related to the high vacuum operation of a TEM as well as the requirement of electron transmission through the sample, a prototype battery must be sealed with thin membrane that enables the electron transmission at the interested region. It is known that electrolytes based on ionic liquid have a low vapor pressure. Therefore, it is generally expected that using ionic liquid as electrolyte, the prototype battery may be operated in vacuum without sealing the whole system using a thin membrane. In this work, we report our exploratory work on developing in-situ TEM devices that will eventually enable direct and high spatial resolution observation of the structural evolution of the interface between the electrolyte and the electrode materials. In a model experiment, a prototype Li-ion battery was developed in the system of using SnO<sub>2</sub>

nanowire as anode, an air stable salt LiTFSI in a hydrophobic ionic liquid as electrolyte, and LiCoO<sub>2</sub> as cathode. Focused ion beam (FIB) manipulation of a single nanowire enables the assembling of a prototype battery. Furthermore, due to the low vapor pressure of the ionic liquid, the whole system can be directly loaded into a TEM without sealing. The interface across the solid-ionic liquid was studied during charging and discharging using TEM imaging and electron energy loss-spectroscopy (EELS). By comparing these results with those obtained from batteries based on coin cell design, several challenges were identified. These results will be discussed along with the future research directions.

4:40pm **IS+AS-ThA9 Characterizing Solid Oxide Fuel Cells during Electrochemical Operation Using Ambient Pressure XPS**, *F. El Gabaly, A.H. McDaniel*, Sandia National Laboratories, *M. Grass, Z. Liu, H. Bluhm, Z. Hussain*, Lawrence Berkeley National Laboratory, *G.S. Jackson, C. Zhang, S.C. Decaluwe*, University of Maryland, College Park, *K.F. McCarty, M.A. Linne, R.L. Farrow*, Sandia National Laboratories

Electrochemical systems for energy applications are hampered by lack of fundamental measurements and understanding of ion transport and interfacial charge transfer mechanisms. Electrochemical devices based on the conduction of O<sup>2-</sup> anions through a solid electrolyte, such as a solid oxide fuel cell (SOFC) or electrolyzer (SOEC), have great potential for both clean, efficient power generation and efficient production of fuels such as hydrogen or synthesis gas. The essential physical phenomena that govern reaction and charge transfer across material interfaces are poorly understood. The ability to directly observe changes in chemical composition and elemental oxidation state at surfaces and interfaces under electrochemically active conditions will provide insight into such processes. Here, we report in situ measurements of Ni and Pt patterned thin films (300nm) electrodes in solid-oxide electrochemical cells using ambient pressure X-ray photoelectron spectroscopy[1] (APXPS, Beamline 11.0.2 of the Advanced Light Source, Lawrence Berkeley National Laboratory). This novel setup provides quantitative information about the elemental surface composition, local surface potential in the yttria-stabilized zirconia electrolyte, and changes in elemental oxidation state as a result of electrochemical and thermochemical activity occurring under relevant operating conditions: typically 0.25 Torr of hydrogen and 0.25 Torr of water, T=1023K, and under applied bias potential. Chemical changes on the fuel cell electrodes under different electrochemical operation will be discussed, as well as the existence of transient species that could help reveal where and how the charge-transfer mechanism is occurring.

#### References

[1] D.F. Ogletree, H. Bluhm, G. Lebedev, C.S. Fadley, Z. Hussain, M. Salmeron, *Rev. Sci. Instrum.* 73 (2002) 3872.

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# Friday Morning, November 13, 2009

## In Situ Microscopy and Spectroscopy: Interfacial and Nanoscale Science Topical Conference Room: C4 - Session IS+AS-FrM

### In-Situ Microscopy and Spectroscopy: Dynamic Nanoscale Processes

**Moderator:** C.M. Wang, Pacific Northwest National Laboratory

8:20am **IS+AS-FrM1 In Situ Atomic-Scale Imaging of an Oxide Supported Catalyst during a Redox Change:  $WO_x$  /  $\alpha$ - $Fe_2O_3$  (0001).** Z. Feng, Northwestern University, J.W. Elam, Argonne National Lab, C.-Y. Kim, Canadian Light Source Inc., Z. Zhang, Argonne National Lab, M.J. Bedzyk, Northwestern University

Ultrathin metal-oxide layers deposited onto oxide surfaces have wide applications in catalysis and chemical sensing. Supported tungsten oxides are among these. If the atomic-scale geometrical and electronic surface structure of  $WO_x$  could be predicted, this would impact our understanding of numerous chemical processes. As a model catalytic system, atomic layer deposition (ALD) grown  $WO_x$  on hematite (0001) was used for finding the positions of W with respect to the support lattice and its sensitivity to the reduction-oxidation (redox) cycle. AFM is used to study the surface morphology changes. X-ray fluorescence and in situ X-ray standing waves (XSW) are used in combination to determine the geometric structure changes during the redox reaction. The XSW results for 1/3 ML W show that W cations on the surface occupy different positions in the as-deposited, oxidized and reduced states. The ALD as-deposited W shows strong correlation vertically but no correlation laterally. Oxidization causes the W ordered and they occupy some special adsorption sites. However, in the reduced state, W cations change their adsorption sites. Atomic density maps created from in situ XSW measurements give us direct information for the W cations surface site location. Finally, X-ray photoelectron spectroscopy (XPS) is used to correlate the W oxidation state(s) with the above redox induced structural changes. A model is proposed to explain the reversible geometrical/electronic structure changes during this redox reaction.

8:40am **IS+AS-FrM2 The Surface Kinetics of the Initial Oxidation Stages of Cu Alloys.** Z. Li, J.C. Yang, University of Pittsburgh

We are studying the dynamics of the initial and transient oxidation stages of a metal and alloys with in situ ultra-high vacuum (UHV) transmission electron microscopy (TEM). We have previously demonstrated that the formation of epitaxial  $Cu_2O$  islands during the transient oxidation of  $Cu(100)$ , (110) and (111) films bear a striking resemblance to heteroepitaxy, where the initial stages of growth are dominated by oxygen surface diffusion and strain impacts the evolution of the oxide morphologies. We are presently investigating the early stages of oxidation of  $Cu-Au$  and  $Cu-Ni$  as a function of oxygen partial pressures and temperatures. The addition of a secondary non-oxidizing element, Au, revealed a self-limiting growth due to the depletion of Cu near the oxide island that significantly slows down the oxide growth as well as lead to an unusual dendritic shape, limiting its ability to form a uniform protective oxide. The  $Cu-Ni$  alloys show more complex behavior, where the two components are 100% solid-soluble down to  $\sim 300^\circ C$  but  $Cu_2O$  and  $NiO$  show limited miscibility. Nickel oxide, which has the cubic NaCl crystal structure, has a more negative standard free energy of formation than  $Cu_2O$ , which is simple cubic, and is expected to form more readily. In this case, depending on the environmental  $pO_2$ , either one or both components of the alloy will oxidize, thus enabling a systematic determination of the effects of compositional and phase development during oxidation. We noted remarkable differences between  $Cu-Ni$  oxidation and our past observations of  $Cu$  and  $Cu-Au$  oxidation: 1) a second rapid nucleation of compact and dense oxide islands occurred and 2) polycrystalline oxides formed, where only cube-to-cube epitaxial  $Cu_2O$  islands nucleated on  $Cu(001)$  and  $CuAu(001)$  for all temperatures and pressures studied. The surface segregation of  $Cu$  and  $Ni$  towards or away, respectively, from the alloy surface during oxidation could disrupt and cause polycrystalline oxide formation. In addition to being excellent model systems for understanding environmental stability of metal alloys, knowledge of the oxidation behavior of  $Cu$ -based alloys is also of practical interest in diverse areas, such as electronics, functional oxides and catalysis.

9:00am **IS+AS-FrM3 In-Situ Aberration Corrected Transmission Electron Microscopy.** T.C. Isabell, J. Brink, B.L. Armbruster, M. Kawasaki, JEOL USA, Inc. **INVITED**

Few electron optical inventions have revolutionized the TEM/STEM as profoundly as the spherical aberration (Cs) corrector. Characterization of technologically important materials increasingly needs to be done at the atomic or even sub-atomic level. This characterization includes determination of atomic structure as well as structural chemistry. With Cs correctors the sub-Ångstrom imaging barrier has been passed, and fast atomic scale spectroscopy is possible. In addition to improvements in resolution, Cs correctors offer a number of other significant improvements and benefits.

One such benefit is that a larger pole piece gap can be used in the TEM, while still achieving sub-Ångstrom image resolution. This means that there is more room around the sample for in-situ experimentation. This opens the door to a whole realm of dynamic experiments, done on a spatial scale never before possible.

There are a few ways in which in-situ experiments in the TEM can be carried out. The TEM can be dedicated to in-situ experimentation and modified to include an environmental cell around the specimen. Through a differential pumping system, the pressure around the sample can be modified and with gas injection systems, the chemistry around the sample can be controlled. Such E-cell TEM systems have existed for years, but recent improvements in design have expanded the usefulness of such systems. Modern E-cell TEMs are capable of not just TEM imaging, but also energy loss spectroscopy (EELS), scanning transmission electron microscopy (STEM) and in some cases energy dispersive spectroscopy (EDS). However, in fully dedicated E-cell TEMs, scanning techniques and EDS may be geometrically limited.

Alternatively, specially designed TEM specimen holders can be used in a conventional TEM for in-situ work. A variety of environmental holders have been developed for these kinds of experiments, including: heating, cooling, straining, and indentation holders; probe holders for electrical measurements; holders with an enclosed environmental cell so that the specimen can be examined under different gases and or liquids; and even holders with an integrated SPM tip for simultaneous TEM/SPM observation of the specimen. MEMS devices are being used for some of these holders to incorporate things such as rapid heating into the specimen holder.<sup>1</sup> These holders can be used to study transport phenomena across interfaces, sintering phenomena in nanoparticles, and elevated temperature studies of catalysts.<sup>2,3</sup>

<sup>1</sup> J. Damiano, D.P. Nackashi and S.E. Mick; *Microsc Microanal* 14(Suppl 2) 1332, 2008.

<sup>2</sup> M. Briceno, et al., *Microsc Microanal* 14(Suppl 2) 1336, 2008.

<sup>3</sup> J. Liu, J. Wang, L.F. Allard; *Microsc Microanal* 14(Suppl 2) 262, 2008.

9:40am **IS+AS-FrM5 Probing Interfacial Atomic and Electronic Structures at Atomic Resolution.** J.-M. Zuo, University of Illinois - Urbana-Champaign **INVITED**

Interfaces are important because they are essential for the function of materials, especially for nanomaterials. New research in oxide thin-films also shows that interfaces can be used to generate new electronic structures. However, interface characterization is always a challenge. Here, I will present our progress in probing atomic structure and electronic structure of interfaces based on aberration corrected scanning transmission electron microscopy and electron energy loss spectroscopy (EELS). Specifically I will cover two topics, one is the epitaxial interface between metal nanocrystals and oxides and the other is atomic scale oxide superlattices. I will illustrate the resolution of the aberration corrected electron microscopy and EELS, and what we have learnt from these characterizations.

10:20am **IS+AS-FrM7 Bringing Chemical Reactions to Life: Environmental Transmission Electron Microscopy (ETEM).** B. Freitag, D. Stokes, D. Hubert, FEI Company, The Netherlands **INVITED**

Electron microscopy can provide more than just static observations and characterization of materials. For example, the environmental transmission electron microscope (ETEM) enables the synthesis of materials in the TEM, and allows us to study dynamic behavior under the influence of different gases and temperatures, while maintaining atomic resolution capabilities. By varying the temperature, pressure and composition of the gaseous environment, it is possible to directly interrogate chemical processes using both imaging and spectroscopic techniques. This allows a deep understanding of the mechanisms and kinetics of reactions at the nanoscale, as evidenced by the growing body of literature (see, for example [1-6]).

The most recent addition to the Titan S/TEM family is specifically designed for ETEM studies, with a pressure range of up to 4 kPa (40mbar, 30 torr) of gas at the specimen area and a wide range of temperatures. This special microscope is equipped with a gas sensor and a plasma cleaner and can be operated in non-ETEM mode with the standard sub-Angstrom specifications of a conventional Titan. Figure 1 demonstrates imaging performance for a nitrogen gas pressure  $p = 500$  Pa (5 mbar, 3.75 torr), showing an information transfer of  $1.2 \text{ \AA}$ , obtained for a gold specimen in an aberration-corrected ETEM. In this talk the performance of the ETEM and application results on chemical reactions are presented.

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11:00am **IS+AS-FrM9 In-situ TEM Investigation of Nanoscale Deformation Mechanisms in Lubricious Thin Films.** *A. M'ndange-Pfupfu, A. Merkle*, Northwestern University, *O. Eryilmaz, A. Erdemir*, Argonne National Laboratory, *L.D. Marks*, Northwestern University

The field of tribology - the study of contacting surfaces in relative motion - has long suffered from the problem of buried interfaces, forcing researchers to conduct experiments completely blind to the underlying mechanical deformation and structural processes that dictate friction behavior. Using a unique in-situ TEM nanomanipulation technique, we can dynamically observe the sliding interface at the single asperity level. With this method, we can deeply probe the effects of film composition on surface behavior and by extension, on the tribology and wear properties of such films.

In particular, we are interested in the nanoscale deformation mechanisms in lubricious thin films, particularly highly-ordered pyrolytic graphite, diamond-like carbon (DLC), and molybdenum disulfide (MoS<sub>2</sub>). The manner in which the material responds to an applied stress is not only of fundamental interest, but of practical importance as device design shrinks to ever-smaller dimensions.

Using our in-situ approach, we have access to all the instrumentation of the TEM. With HOPG and MoS<sub>2</sub>, we can use electron diffraction to look at the structural deformations in the graphitic grains as a function of the type and magnitude of applied stress. We have also looked at the phase transformation usually known as graphitization seen in DLC films. The bonding configuration at the surface has been shown to play a significant role in nanotribological properties, along with experimental and growth parameters such as the relative amount of hydrogen present at the surface. By using electron energy loss spectroscopy combined with high resolution imaging, we can look at the effect of film hydrogenation on the speed of the phase transformation, which is useful for both applications and for determining the actual mechanism involved.

11:20am **IS+AS-FrM10 Real-time Observation of Non-diffusive Reactive Spreading of Gold on Silicon.** *N. Ferralis*, University of California, Berkeley, *F. El Gabaly*, Sandia National Laboratories, *A.K. Schmid*, Lawrence Berkeley National Laboratory, *R. Maboudian, C. Carraro*, University of California, Berkeley

The spreading dynamics of a bilayer gold film propagating outward from gold clusters, which are pinned to the clean Si(111) surface, are imaged in real time using low energy electron microscopy. By monitoring the morphological evolution of the Au-Si interface at fixed temperature, a linear dependence of the spreading radius of the interface as function of time is found. The measured spreading velocities in the temperature range of  $800 < T < 930$  K varies from below 100 pm/s to 50 nm/s. We show that the linear time dependence in the formation of the interface between the gold silicide and the clean Si surface is a direct consequence of the large difference in surface energy between the two phases. In atomistic terms, the dynamics of the spreading is reaction-attachment limited, and it appears to be regulated by the structural reconstruction of gold silicide that takes place at the interface.

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