In Situ Microscopy and Spectroscopy: Interfacial and Nanoscale Science Topical Conference
Room: 310 - Session IS+SY+SS-WeM

In Situ Spectroscopy – Interfacial Science and Catalysis
Moderator: D.R. Baer, Pacific Northwest National Laboratory

8:00am **IS+SY+SS-WeM1 Probing the Electrochemistry of Ceria in Solid-Oxide Fuel Cell Anodes under Operation using Ambient-Pressure XPS**, ***H. Bluhm***, *J.T. Newberg, Z. Liu, Z. Hussain,* Lawrence Berkeley National Laboratory, *S.C. DeCaluwe, C. Zhang, G.S. Jackson,* University of Maryland, College Park, *F. El Gabaly, R.L. Farrow, K.F. McCarty, M.A. Linne, A.H. McDaniel,* Sandia National Laboratories

Solid-oxide fuel cells (SOFCs) are an important technology for converting chemical energy to electrical energy. A compelling advantage of SOFCs is the ability to utilize fuels such as hydrogen, synthesis gas, and hydrocarbons. In a conventional SOFC, selective catalytic and charge transfer processes produce O^{2-} ions at the cathode/electrolyte interface, which then diffuse through a dense electrolyte to an anode/electrolyte interface where adsorbed fuel species are oxidized. Ceria (CeO_2), a mixed conductor capable of transporting both O^{2-} ions and electrons, is being considered as a coke-resistant anode catalyst to improve SOFC performance. A key unknown about ceria-catalyzed anodes is the cerium (Ce) oxidation state during fuel cell operation. Cell performance is critically affected by the Ce oxidation state because Ce^{3+} and Ce^{4+} states coexist in CeO_2, and both electronic and ionic conductivities are determined by the abundance of Ce^{3+}. To exploit the potential of ambient-pressure XPS to characterize functioning electrochemical devices, we have fielded an SOFC experiment on beamline 11.0.2 at the Advanced Light Source. A single chamber cell was created by patterning working and counter electrodes from ceria and platinum atop single crystal yttria-stabilized zirconia (YSZ) electrolyte. The cell was characterized in atmospheres of H_2/H_2O and $H_2/O_2/H_2O$ under forward and reverse polarization at approximately 973 K and 0.5 Torr. Standard chronoamperometric and impedance measurements were conducted simultaneously with ambient-pressure XPS. A focused x-ray beam (diameter < 0.1 mm) was used to spatially resolve changes in the Ce oxidation state as a function of position between counter and working electrodes under positive and negative bias. Electrochemically induced changes in the Ce oxidation state were directly observed and were dependent upon electrode polarization and proximity to electrochemically active regions. In addition, the oxidation state and surface potential of the YSZ electrolyte were also characterized. Implications of our findings on understanding the electrochemical mechanisms of SOFC operation with ceria anodes will be discussed.

This research was supported by the U. S. Department of Energy under Contract No.DE-AC04-94AL85000 (Sandia) and DE-AC02-05CH11231 (LBNL). UMD participants were supported by the Office of Naval Research under Contract No: N000140510711.

8:20am **IS+SY+SS-WeM2 In-situ Dynamics of CO Oxidation on Pt(110) with Ambient Pressure XPS**, *Z. Yang, F. Aksoy, Z. Liu,* Lawrence Berkeley National Laboratory, *H. Kondoh,* Keio University, Japan, *P. Ross,* Lawrence Berkeley National Laboratory, ***B. Mun***, Hanyang University, Korea

Considering the recent increasing demands of improved catalytic materials in energy industry, the understanding clear mechanism of catalytic reactions at an atomic scale level has become more critical. Especially, the formations of oxide on transition metal surface have been actively studied due to its importance in fundamental understanding of heterogeneous catalytic reactions on metal surfaces. In particular, the study of surface oxide on Pt [110] received much attention due to its unique surface reconstruction under high pressure reaction conditions. Previously, with the combinations of high pressure STM and in-situ x-ray diffraction, the formation of surface Pt oxide is observed when the reaction rate is enhanced, and showed the surface oxide formed is stable with carbonate species.[1,2] In this work, using the ambient pressure XPS (AP XPS) and mass spectrometer, the in-situ dynamics of CO oxidation on Pt [110] surface are discussed under close to the realistic condition. Under the reaction conditions (T=420K) with the pressure of CO and O gases at 450 mTorr in the AP XPS chamber, our results show that a) the chemisorbed oxygen is not stable under the reaction conditions, b) there is no formation of surface oxide on Pt surface under our reaction conditions.

[1] B.L.M. Hendrikson and J.W.M. Frenken, Phys.Rev. Lett. 89, 046101(2002)

[2] M.D. Ackermann et al.,Phys.Rev. Lett. 95, 255505(2005).

8:40am **IS+SY+SS-WeM3 Medard W. Welch Award Lecture: Novel X-ray Photoelectron Spectroscopy Techniques for In Situ Studies of Surfaces in Equilibrium with Gases in the Torr Pressure Regime: Application to Catalysis and Environmental Sciences**, ***M. Salmeron****, Lawrence Berkeley National Laboratory **INVITED**

X-ray photoelectron spectroscopy (XPS) ideally suited to investigate the chemical nature of surfaces. Due to the scattering of eletrons by gas molecules XPS is in generally performed under high vacuum conditions. However, because of thermodynamic and/or kinetic limitations, the surface chemical state observed under vacuum is not necessarily the one under the pressures that are relevant to catalysis and the environment (Torr to atmosphere). We developed a electrostatic lens system combined with differentially-pumped chambers that permits operation at pressures of up to 10 Torr. I will describe this ambient pressure XPS apparatus and show recent applications to studies of oxidation and heterogeneous catalytic reactions. I will also show how the technique can solve and advance our fundamental knowledge of surfaces in environmental science studies, particularly in the presence of water vapor.

9:20am **IS+SY+SS-WeM5 Nano Scale X-ray Absorption Spectroscopy of In Situ Modified Samples using Scanning Transmission X-ray Microscope**, ***T. Tyliszczak***, Lawrence Berkeley National Laboratory **INVITED**

Observation and spectroscopy of in situ chemical reactions on nanoscale is important but not easy task. It is important in many fields, especially in research of heterogeneous catalysts. Typically, transmission electron microscopy has been used under in situ conditions, but the strict low pressure requirements for this technique prevent it from being carried out under catalytically relevant conditions. Recently however, by using a specially designed microreactor, promising TEM experiments have been performed under 1 bar conditions but with a limitation of gases which could be used.[1] Other techniques include STM, fluorescence and optical microscopy. Most of these techniques allow imaging of intermediate steps of reactions with limited information about reaction chemistry. Scanning Transmission X-ray Microscopy (STXM) with relatively good spatial resolution of 20-30 nm, high chemical sensitivity and much lower restriction on the environment of a sample is promising to provide new insides into the catalytic reactions. By using soft X-rays (130 -2000 eV) as a microprobe, it is possible to study both the active phase of the catalyst, through absorption edges of the inorganic species, and the organic, reactant phase of the catalyst through the absorption edges of carbon, oxygen and nitrogen. While the maximum spatial resolution of STXM is still significantly worse than for example STEM-EELS, there are important advantages in application STXM, most notably the superior spectral resolution and the reduced radiation damage in the study of softer core hole edges (C, N, O K-edges) and hydrated samples. Bell et al.[2] first demonstrated the use of STXM for the study of a catalytic material under in situ conditions. Their cell design allowed sample treatments in gases up to 260 °C. E. de Smit et al.[3] used modified ETEM cell to in situ studies of a complex iron oxide based Fischer-Tropsch catalyst. They were able to heat the sample up to 500oC at gas pressure up to 1.2 bar opening a way to study real catalyst normal conditions. The cell, manufactured as a microelectromechanical system (MEMS), basically consists of a 500 * 500 mm reactor chamber connected by micrometer-sized gas-flow channels. Two amorphous Si3N4 optical windows, etched down to a thickness of 10 nm in certain places, separate the reactor from the outside environment. The thickness of the reactor, thus gas path length, is only about 50 mm, and therefore ensures minimum attenuation of the X-ray light by the gas phase molecules. Spacers, placed between the windows prevent the windows from sticking together. The sample is loaded by flowing a powder suspended in a solvent (e.g. ethanol) through the reactor and subsequent drying. After drying, the sample is supported on the SiNx windows. E. de Smit et al were able to track reaction steps measuring changes in chemical state of iron and oxygen. They also investigated a role of carbon in the reaction. Progress in technical development of reaction cell and increasing resolution of the x-ray microscope provide opportunity to investigate gas - solids or liquid - solids in situ, in relevant conditions on nanometer scale.

[1] J. F. Creemer, S. Helveg, G. H. Hoveling, S. Ullmann, A. M. Molenbroek, P. M. Sarro and H. W. Zandbergen, Ultramicroscopy, In Press, Accepted Manuscript.

[2] I. J. Drake, T. C. N. Liu, M. Gilles, T. Tyliszczak, A. L. D. Kilcoyne, D. K. Shuh, R. A. Mathies and A. T. Bell, Review of Scientific Instruments, 2004, 75, 3242-3247.

[3] E. de Smit , I. Swart, J. F. Creemer , G. H. Hoveling, M. K. Gilles , T. Tyliszczak, C. Morina, P. J. Kooyman, H. W. Zandbergen, B. M. Weckhuysen and Frank M.F. de Groot, Nature, submitted manuscript.

***** Medard W. Welch Award Winner

10:40am **IS+SY+SS-WeM9 In Situ Synchrotron X-ray Study of the Synthetic Processes for Inorganic Solid Oxide Nanomaterials**, *Y. Mao, **J. Dorman**, J.P. Chang*, University of California at Los Angeles

Nanostructured crystalline inorganic solid oxides show various intriguing properties and process many important technological applications. To better control the property and device performance of materials, growth kinetic and mechanistic information of structure changes should be pursued to provide feedback for the development of new “designer” materials to meet the challenges of the future. Time-resolved in situ experimentation represents the most likely means, especially with the synchrotron radiation as the x-ray source due to its high energy flux. In this study, we focus on advanced luminescent nanomaterials, since they have practical applications in nearly all devices involving the artificial production of light and are applicable in nanoscaled electronics, photonics, display and advanced bioanalysis. In this talk, we present our recent investigation by in-situ time-resolved synchrotron x-ray diffraction (XRD) and absorption spectroscopy (XAS) on the synthesis of rare-earth doped metal oxide nanostructures, including Er:Y_2O_3 nanotubes and nanoparticles and Er: $La_2(Zr_xHf_{1-x})_2O_7$ nanoparticles, by hydrothermal and molten-salt syntheses.[1,2,3] Our results demonstrate that in situ XRD and XAS data support each other. For the hydrothermal synthesis of Er:$Y(OH)_3$ nanotubes, the hydroxide phase starts to form immediately and continues to grow. For the dehydration process from Er:$Y(OH)_3$ nanotubes to Er:Y_2O_3 nanotubes, the dehydration starts at ~250°C and completes at 450°C and an intermediate oxyhydroxide phase was found for the first time. Furthermore, the in situ XRD study provided guidance on the selection of proper annealing temperature for the molten salt synthesis of Er:Y_2O_3 and Er: $La_2(Zr_xHf_{1-x})_2O_7$ nanoparticles. Their growth kinetics will be obtained from further investigation of these processes under different ramp rates and reaction temperatures.

[1] Mao, et al. Synthesis and luminescence properties of erbium-doped Y_2O_3 nanotubes, J. Phys. Chem. C, 112, 2278 (2008).

[2] Mao, et al. Molten salt synthesis of highly luminescent erbium-doped yttrium oxide nanoparticles, submitted (2008).

[3] Mao, et al. $La_2Zr_2O_7$ and $La_2Hf_2O_7$ nanoparticles from single-source complex precursors: kinetically modified synthesis and luminescent properties, submitted (2008).

11:00am **IS+SY+SS-WeM10 Surface Chemistry of Model Solid Oxide Fuel Cells Studied In-Situ by Synchrotron Based Photoemission Microscopy and Spectroscopy**, ***K. Adib**, M. Backhaus-Ricoult, T.P. St. Clair,* Corning Incorporated, *B. Luerssen,* Justus Liebig Universitaet, Germany, *L. Gregoratti, A. Barinov*, Sincrotrone Elettra, Italy

We have used synchrotron based X-ray photoemission spectroscopy (XPS) and scanning photoemission microscopy (SPEM) to study the surface compositions of model solid oxide fuel cells containing $La_xSr_{1-x}MnO_3$ (LSM) cathode and yttrium-stabilized zirconia (YSZ) electrolyte under various oxygen pumping conditions at approximately 650°C and an oxygen partial pressure of $5x10^{-7}$ mbar. SPEM in the vicinity of the LSM/YSZ interface indicates depletion of Mn atoms from the LSM surface and their accumulation on the YSZ surface with increasing cathodic bias. XPS indicates that the accumulation of Mn on the YSZ is accompanied by reduction in the oxidation state of Mn. Within a wide range of applied voltage these changes are reversible. XPS of oxygen core levels also indicates that under cathodic bias, during which oxygen is incorporated from the surrounding gas into the cathode and pumped through the electrolyte, an additional oxygen species is present on the surface of LSM. The concentration of this species increases with increasing cathodic bias and we tentatively assign this species to surface oxygen as distinct from lattice oxygen. On the YSZ surface, no such change in the concentration of the surface oxides with cathodic bias was detected emphasizing the role of LSM in enhanced adsorption of oxygen.

11:20am **IS+SY+SS-WeM11 Organic Solar Cells and Microgels: Examples of In Situ Applications of Soft X-ray Microscopy**, ***H. Ade***, North Carolina State University **INVITED**

Soft x-ray microscopy has achieved a spatial resolution of ~ 30-40 nm. At the same time, soft x-rays are penetrating enough to investigate samples sandwiched between thin silicon nitride membranes or thin metal layers. This allows the investigation of wet samples or samples sandwiched between thin electrodes. When coupled with Near Edge X-ray absorption Fine Structure (NEXAFS) spectroscopy, unique characterization capabilities results that range from compositional mapping, to charge state determination and induced current measurements. This presentation will review the state-of-the-art of NEXAFS microscopy. The focus will be on a range of in-situ applications and most extensively on the characterization of microgels and organic solar cells.

In Situ Microscopy and Spectroscopy: Interfacial and Nanoscale Science Topical Conference
Room: 310 - Session IS+NS+TR-WeA

In Situ Microscopy and Spectroscopy – Interfacial Science and Catalysis
Moderator: I. Petrov, University of Illinois at Urbana-Champaign

1:40pm **IS+NS+TR-WeA1 Large Sample Volume, Constant Flow, High Temperature MAS Probe for Catalytic Systems**, ***J.J. Ford***, *J.Z. Hu, J.A. Sears, J.H. Kwak, D.W. Hoyt*, Pacific Northwest National Laboratory

We have recently finished construction of a new NMR probe to study catalytic systems under conditions where the reactions actually occur. The probe uses a 9.5 mm commercially available MAS rotor system and is built to operate in a 500 MHz wide bore magnet. An integrated heater assembly is able to raise the sample temperature to 400°C while the sample is spinning up to 3.5kHz. The rotor and stator assembly have been modified to allow a continuous flow of reactants through the rotor while it is spinning and at temperature. The carrier gas of either N2 or He can carry reactants into the probe and move products out of the probe. Inserts for the rotor diffuse the gas stream over the catalyst bed and collect it on the other side. This allows steady state NMR measurements to be made under conditions comparable to those in typical catalytic environment – high temperatures and a steady influx of reactants and exhaust of products. The high sensitivity from this larger sample volume probe allows 13C observation at natural abundance. Performance test results will be presented, including an investigation of the reaction mechanisms of the carbonylation of dimethyl ether to methyl acetate on mordenite. This work has been supported by an intramural capability grant from EMSL and a DOE-Catalyst grant.

2:00pm **IS+NS+TR-WeA2 Photoelectron Emission Microscopy during CO Oxidation on Non Reconstructing Noble Metal Surfaces**, ***S. Wehner***, *S. Karpitschka,* Universität Bayreuth, Germany*, P. Hoffmann,* Hahn-Meitner-Institut Berlin, Germany*, Y. Burkov, D. Schmeißer,* Technische Universität Cottbus, Germany*, H.R. Brand, J. Küppers*, Universität Bayreuth, Germany

The catalytic CO oxidation on Iridium(111) and Palladium(111) surfaces was investigated experimentally under ultrahigh vacuum (UHV) conditions using photoelectron emission microscopy (PEEM) to visualize surface species. The underlying reaction-diffusion system based on the Langmuir-Hinshelwood mechanism was analyzed numerically. The effect of noise on this bistable surface reaction was examined for both surfaces. In a surface science experiment the effects on product formation detected by mass spectroscopy and the development of spatio-temporal patterns on the surface were explored. The influence of noise on the reaction rates and the formation of spatio-temporal patterns on the surface was analyzed by superposing noise of Gaussian white type on the feed gas composition, characterized by the molar fraction of CO Y (variance $(\Delta Y)^2$), which represents multiplicative and additive noise. CO- and oxygen-covered regions are visible in PEEM images on both surfaces as brighter resp. darker areas as a consequence of their work function contrast. In the Iridium case islands of the adsorbate, corresponding to the globally stable branch, are formed in a background of the other adsorbate. The long transient times are the result of the extremely slow domain wall motion of these islands (around 0.05 μm s^{-1}). For small noise only a few islands nucleate and grow until they merge and finally fill the whole surface. With increasing noise the number of islands increases and their maximum size decreases. At constant ΔY the island wall velocity and the number of islands increases when Y approaches the hysteresis boundary. The island density increases with noise, but the wall velocity is independent of applied ΔY. In the Palladium case quasi-periodic breakdowns of the CO_2 with an interval of some thousands of seconds are recorded. These breakdowns are connected with very large patterns on the surface. Their domain wall motion is very fast (about 10 μm s^{-1}). This long quasi-periodic behavior vanishes, already when small noise is superposed. For larger noise the CO oxidation reaction on both surfaces shows bursts and switching in the product CO_2 rate and the recorded PEEM images.

2:20pm **IS+NS+TR-WeA3 Catalytic Raman Spectroscopy: Structure and Activity during Reaction**, ***M.A. Bañares***, *S.J. Khatib, O. Guerrero-Pérez, M.V. Martínez-Huerta, A.E. Lewandowska*, Catalytic Spectroscopy Laboratory, CSIC, Spain **INVITED**

Catalysts with large surfaces are much more complex than the model single crystals. To single out the active site under real working conditions of the catalyst is an enormous task. It requires a combination of techniques and the development or adaptation of techniques, which allow measurements under catalytic conditions (high temperatures and high pressures). This is the field of in situ spectroscopy. We have recently developed a new methodology that combines the determination of catalyst activity/selectivity and its molecular structure in a single experiment.[1,2] We have named this methodology "operando" (Latin for "working"). The presentation will cover Raman studies to assess structure-activity relationships on supported oxides (namely V, Cr, Mo) during alkane and ammonia activation (ammoxidation). In addition, a combination of in situ Raman, XANES, and EPR spectroscopies is used to study the nature of the interaction between V and oxides supports. On most oxide supports, the redox cycle involves reversible reduction of supported vanadia sites. Ceria support behaves differently, though. Surface V5+ species strongly interact with ceria support promoting a reduction of surface Ce4+ to Ce3+. Upon heating or during reaction surface vanadia reacts with ceria support forming a CeVO4 phase. The active site appears to be V5+–O–Ce3+ for both systems. The redox cycle for oxidative dehydrogenation appears to be associated with Ce, rather than with V sites.[3]

ACKNOWLEDGMENT. The support of the Spanish Ministry of Education and Science (CTQ2005-02802/PPQ)

[1] "Operando Raman study of alumina-supported Sb-V-O catalyst during propane ammoxidation to acrylonitrile with on line activity measurement", M. O. Guerrero-Pérez and M. A. Bañares, Chem. Commun. 12, 1292 (2002).

[2] Miguel A. Bañares, Catal. Today 100, 71 (2005) (SPECIAL ISSUE NUMBER 100)

[3] M.V. Martínez-Huerta, J. M. Coronado, M. Fernandez-García, A. Iglesias-Juez, G. Deo, J.L.G. Fierro, M.A. Bañares, J. Catal. 225 (2004) 240-248

3:00pm **IS+NS+TR-WeA5 Understanding Nanoparticle Behavior in Solution: Combining Real-Time In Situ with Selective Ex-Situ Measurements to Study Transformations of Nanoparticulate Iron**, ***D.R. Baer***, Pacific Northwest National Laboratory*, P.G. Tratnyek, J.T. Nurmi,* Oregon Health & Science University, *J.E. Amonette, P. Nachimuthu, C.M. Wang, M.H. Engelhard,* Pacific Northwest National Laboratory*, A. Sharma, Y. Qiang*, University of Idaho

In many circumstances nanoparticles are transformed by their environment. These transformations may impact particle structure, involve the formation of surface or contamination layers or alter important particle chemical or physical properties critical for specific applications. In our studies of nanoparticulate iron in aqueous solution related to contaminant transport in the environment, we need to understand the nature of the transformations and the time frame over which they occur. We are also working to develop methods to control (increase or decrease) the rate of these changes. We find that real-time in situ measurements are essential in addition to some batch ex-situ measurements to fully characterize the transformation. Determining minimum combination of in-situ and ex-situ measurements that provides the essential information is a challenge. We have used electrochemical potential and gas production (hydrogen production) to observe the real-time dependence of particle reaction properties. These have been correlated with batch ex-situ measurements, often involving anaerobic sample handling, of surface composition (XPS), particle phase composition and structure (XRD and TEM) and reaction rates with probe molecules (carbon tetrachloride). Real time in situ measurements are increasingly important as we develop ways to alter the particles with the intent of controlling the transformation rate of particles in aqueous solution. Initial data indicates that sulfur and transition metal doping of the particles significantly alters the overall reactivity and the interaction with contaminants. We are currently examining the impact of sulfur and transition metal additions as well as changes in oxide shell thickness on the reaction lifetime of core-shell iron nanoparticles. Because of a need to provide additional types of time-dependent information we are applying microbeam XRD and TEM in closed cells to examine these particles as they change in solution. This work is supported by the US Department of Energy Offices of Basic Energy Science and Biological and Environmental Research. A portion of the work has been conduced the the EMSL, a US DOE national user facility.

4:00pm **IS+NS+TR-WeA8 Dynamics of Catalytic Nanoparticles**, ***A. Datye***, *A. Delariva, J. Gabaldon, L.M. Sanders, R. Goeke, Q. Xu,* University of New Mexico, *T. Hansen,* University of New Mexico and Haldor Topsøe A/S, Denmark, *S. Helveg, P. Hansen, B.S. Clausen*, Haldor Topsøe A/S, Denmark **INVITED**

Nanometer sized particles constitute the active phase in heterogeneous catalysts, such as those used in automotive exhaust pollution control, in energy conversion and for synthesis of chemicals. The unique properties of heterogeneous catalysts, their activity and selectivity, depend on the size and composition of nanoparticles. Since catalysts are used at elevated temperatures, these nanoparticles undergo coalescence and ripening leading to particle growth. Understanding and controlling these growth processes is critical since supplies of precious metals (such as Platinum, or Gold) are limited and demand keeps increasing, for example in fuel cells. Fundamental understanding of catalyst deactivation via sintering requires careful experimental work using a combination of ex-situ and in-situ studies. Ex-situ studies allow us to map out global rates and kinetics of particle size evolution. For this purpose, we have used a combination of TEM, STEM, XRD, chemisorption and reactivity measurements. In-situ observations can reveal nanoparticle dynamics and are crucial to bridge the gaps in our understanding, often revealing unexpected events. In this presentation, we will highlight our current state of understanding of sintering phenomena in heterogeneous catalysts. This research is supported by the National Science Foundation.

4:40pm **IS+NS+TR-WeA10 In-situ Transmission Electron Microscopy of Solid-Liquid Interfaces**, ***H. Saka***, Nagoya University, Japan **INVITED**

Most of the industrially important inorganic materials are manufactured from liquid phase. This is true for metallic materials and semiconductors (e.g. Si). Even in the case of ceramic materials, the liquid phase plays an important role in the process of sintering. The performances of the final products of these materials are controlled during the transformation from liquid to solid states. Needless to say, the reaction front of the liquid-to-solid transformation is the interface between the solid, being solidified, and the liquid phases. Thus, in order to manufacture final products with high performance, it is of great necessity to control the solidification process, and this necessitates, in turn, a detailed knowledge of the solid-liquid (S-L) interface, which controls the solidification process. Recently it has become possible to observe S-L interface by an in-situ heating experiment in a transmission electron microscope (TEM), some of which will be presented in this presentation.

Thursday Morning, October 23, 2008

In Situ Microscopy and Spectroscopy: Interfacial and Nanoscale Science Topical Conference
Room: 310 - Session IS+NS+TR+NC-ThM

In Situ Spectroscopy – Dynamic Nanoscale Processes
Moderator: S. Kodambaka, University of California, Los Angeles

8:00am **IS+NS+TR+NC-ThM1 Spatially-Resolved, Surface-Species Concentrations from Electron Reflectivity -- How Graphene Grows on a Metal**, ***K.F. McCarty***, *E. Loginova, P.J. Feibelman, N.C. Bartelt*, Sandia National Laboratories

The rates of many surface processes, and notably of film growth, are governed by the concentrations of mobile adsorbed species. But, few techniques, if any, are available to measure small concentrations of adsorbed species with high spatial resolution. Therefore, the relationship between adsorbates and surface processes typically emerges from indirect observations. Motivated by this limitation, we are developing a technique based on electron reflectivity to obtain local adsorbate concentrations. We measure electron reflectivity changes from the brightness of low-energy electron microscopy (LEEM) images. They yield the local surface-species concentration with high spatial and temporal resolution. This quantitative approach offers the ability to determine the local adsorbate concentrations on heterogeneous surfaces dynamically and under in-situ conditions. We will illustrate the technique's capability with a direct determination of the relationship between mobile carbon adatoms, and the growth of graphene (i.e., of single atomic sheets of graphitic carbon) on Ru(0001), a representative metal. The carbon is supplied by segregation from the bulk metal upon cooling, or by deposition from an evaporator. We find that the reflectivity of low-energy electrons decreases in strict proportion to the concentration of adsorbed, gas-like carbon. By calibrating using known coverages, we can determine absolute adatom concentrations. The graphene growth mechanism was deciphered by simultaneously measuring the instantaneous growth rate of individual graphene islands, and the concentration of surrounding carbon adatoms. The mechanism is very striking and in sharp contrast to metal epitaxy. We found that: the graphene growth rate is limited by carbon atom attachment and not by carbon atom diffusion; the growth rate as a function of supersaturation is highly nonlinear. We will present a model that explains these observations and provides insight into the molecular processes by which graphene grows. Separately, we have determined the carbon adatom concentrations that are in equilibrium with the carbon in Ru's bulk and with graphene, respectively. This information helps understand the competition between the system's three possible carbon configurations: C in bulk Ru, C as adatoms, and C in graphene. This research was supported by the Office of Basic Energy Sciences, Division of Materials Sciences, U. S. Department of Energy under Contract No. DE-AC04-94AL85000.

8:20am **IS+NS+TR+NC-ThM2 Electron Diffraction Characterization of In Situ Deformation of Gallium Oxide Nanobelts**, ***J.M. Vaughn***, *M.E. Kordesch*, Ohio University

A transmission electron microscope fitted with a home-built nano manipulator for in situ mechanical deformation of nanobelts is reported. Nanobelts of beta Ga2O3 are grown by the vapor transport method from gallium metal in an argon gas flow at 950 degrees centigrade. A single 2.5 um wide, approximately 200 nm thick and 10's of microns long belt is deformed by direct contact with the manipulator probe. Deflections of up to 180 degrees are possible without fracture of the belt. A series of TEM diffraction patterns are collected during belt deformation. The diffraction pattern is observed to distort as the belt is deformed. In addition to the distortion of the monoclinic belt diffraction pattern, additional diffraction spots are observed through belt deformation. Analysis of the additional spots and deflection in preexisting spots reveal simultaneous lengthening and contracting in measured planar spacings. This data is modeled by lattice deformations, which allows for such a large deformation of the belt. The lattice deformation model results in the lattice constant 'c' having two simultaneous values for any given diffraction pattern. The maximum simultaneous deformation in 'c' is measured to be 11.3 and 16.3 Angstroms. Lattice constant 'a' behaves similarly with values 5.1 and 7.9 Angstroms. Finally, the lattice deformation model is compared to a plane slipping model, which may also explain the additional spots and deformation.

Funded by a 2005 AVS Undergraduate Research Award.

8:40am **IS+NS+TR+NC-ThM3 Direct Observation of Carbon Nanotubes Formation from Selectively Fabricated Catalyst Particles**, ***R. Sharma***, Arizona State University **INVITED**

Carbon nanotubes (CNT) have many advantageous properties with potential for diverse advanced materials applications if their controlled synthesis can be optimized. For some applications, such as field-emitting displays, in-situ deposition of catalyst particles is an important step for CNT synthesis. Post synthesis characterization of CNTs is frequently performed using transmission electron microscopy (TEM) techniques. Therefore environmental scanning transmission electron microscope (ESTEM) is perfectly suited for in situ observations of nucleation and growth of CNTs. A modern ESTEM, equipped with a field-emission gun (FEG), energy filter or electron energy loss spectrometer, scanning transmission electron microscopy (STEM) coils, and bright and dark field detectors, is a versatile tool for understanding their synthesis process at nanometer level. We have employed a modified Tecnai-F20 ESTEM to understand the catalytic chemical vapor deposition process for CNT synthesis. Time, temperature and pressure resolved digital video imaging is used to determine the effect of synthesis condition on their structure and morphology. Statistical analysis of the CNTs formed under varying synthesis conditions show that 95% yield for SWCNTs can be achieved at 650oC in 1 mTorr of acetylene using Ni as catalyst. We have combined electron beam induced decomposition (EBID) of nonacarbonyl diiron (Fe2(CO)9) to fabricate arrays of Fe particles that are catalytically active for the thermal decomposition of acetylene to form multiwall CNTs. Atomic resolution video images are used to understand the nucleation and growth mechanism from crystalline catalyst particles. Detailed phase transformation of the catalyst particle and CNT growth mechanisms from selectively fabricated Fe particles will be presented.

9:20am **IS+NS+TR+NC-ThM5 Investigating Catalyst Behavior Prior to and during the Growth of Carbon Nanotubes with Environmental Cell TEM**, ***E.A. Stach***, *S.M. Kim, D.N. Zakharov, P. Amama, C. Pint, R.H. Hauge, B. Maruyama*, Purdue University **INVITED**

In order to understand how carbon nanotubes form, one must have a detailed understanding of the size, shape and evolution of the catalysts responsible for their nucleation and growth. In this presentation, we describe our recent studies in understanding the evolution of Fe catalysts deposited on alumina during the so-called supergrowth of carbon nanotubes. These studies rely heavily on the exploitation of the unique capabilities of environmental transmission electron microscopy to observe at the atomistic scale how catalyst nanoparticles transform under varying regimes of temperature and pressure. We will show that modifications of the substrate treatment and carrier gas atmosphere have a strong effect on catalyst coarsening. In particular, we find the presence of H2O – the key ingredient in supergrowth – leads to a reduction in the Ostwald ripening of the Fe catalysts, thereby leading to denser nanotube carpets. Additionally, under conditions identical to those used in supergrowth, we confirm the diffusion of Fe into the Al2O3 supporting layer. This effect could play a significant role in the catalyst surface density during supergrowth, as well as provide another route in which carpet growth may terminate. These studies are correlated with real time TEM observations of the Ostwald ripening rate of Fe nanoparticles on different supports in H2 and H2 + H2O atmospheres, and on the nucleation and growth of the tubes themselves.

10:40am **IS+NS+TR+NC-ThM9 The Large Chamber SEM: A New Tool for Non-Destructive Testing**, ***M. Klein***, VisiTec Microtechnik GmbH Germany

Although conventional SEMs are limiting the size of objects or production equipment to be inspected scanning-electron-microscopes (SEM) are well known instruments for the use in nearly any micro¬technology. A more flexible tool to allow a visual control of micro¬mechanical manu¬facturing, assembling, and testing process is not yet described. Analyzing human behaviour during the visual investigation of objects and adapting this behaviour, lead to a new concept of electron microscopes called Large Chamber Scanning Electron Microscope (LC-SEM) In this case the electron optics is installed within the vacuum chamber and can be positioned freely inside this chamber. This change of kinematics combines conventional SEM´s advantages of high resolution and high depth of focus with the possibility to observe and test micro¬mechanical handling and assembly equipment. Using the LC-SEM allows a new understanding of these processes. The paper describes development, functionality, and applications of this LC-SEM. There are fields of application within the microtechnology and macro¬technology as well. The paper is focused on the use of the LC-SEM within microtechnology, microassembly and micromecha¬tronics. For nearly any process of manufacturing in the microworld a transmission of information to the human macroworld is necessary. For this purpose especially a visual control is important. Optical microscopes are of limited use due to their small magnification and depth of focus (e.g. an optical microscope offers just a depth of focus of 2 µm at an enlargement of 100). Conventional scanning-electron-microscopes (SEM) offer a much better resolution and a better depth of focus but are limited in the size and weight of objects to be inspected because of the usually small vacuum-chambers. Conventional goniometer tables are constructed with a very high precision and for a load carrying capacity up to 20 kg. The load carrying capacity is greatly restricted in that in conventional goniometer tables it is necessary to provide numerous moving guide elements and slide carriages, which for cost reasons are only designed for a moderate load. Therefore an Large Chamber- Scanning Electron Microscope as a tool to support the investigation of microproduction has been developed which opens new fields of application to electron microscopy. Key to the functionality of this microscope is the adaption of human behaviour during the investigation of objects.

11:00am **IS+NS+TR+NC-ThM10 In-situ Electron Microscopy and Spectroscopy Studies of Interfaces in Advanced Li-ion Batteries under Dynamic Operation Conditions***,* ***C.M. Wang****, Z.G. Yang, S. Thevuthasan, J. Liu, D.R. Baer,* Pacific Northwest National Laboratory*, N. Salmon*, Hummingbirds Scientific

Repeated charging and discharging of a Li-ion battery induces microstructural evolutions both at the interface between the electrolyte and the electrode and within the electrode (active materials) due to Li migration. Although it has been established that this structural evolution is responsible for the failure of such batteries, the mechanisms of the microstructural evolution as a function of charging/discharging are not well understood. Advanced diagnostic tools such as electron microscopy along with other surface and bulk sensitive tools, usually in ex-situ mode, have been used to probe into this scientific issue. However, it has been realized that characterizing this interface using an ex-situ capability is a challenge as the materials will be altered during sample preparation and processing and the interface will be stable only under the operating conditions. In-situ capabilities that enable the observation of the structural and chemical changes during the dynamic operation of battery are needed to address this scientific and technological challenge. We have been developing an environmental holder capability for TEM, trying to gain fundamental scientific understanding of the chemical and structural evolution at the interface between the electrolyte and the electrode as well as within the electrodes under the dynamic operation conditions of the Li battery system. In the preliminary research work, we have explored the interface change using TiO2 nanowire as the anode material. Transmission electron microscopy (TEM) imaging, electron diffraction, and electron energy-loss spectroscopy (EELS) were used to probe into these structural evolutions during the operation of the battery.

11:20am **IS+NS+TR+NC-ThM11 The Dynamics of the Initial Oxidation Stages of Cu and Cu Alloys***,* ***J.C. Yang***, University of Pittsburgh **INVITED**

Surface oxidation processes play critical roles in environmental stability, high temperature corrosion, electrochemistry, catalytic reactions, gate oxides and thin film growth as well as fuel reactions. Much is known about oxygen interaction with metal surfaces and about the macroscopic growth of thermodynamically stable oxides. At present, the transient stages of oxidation – from the nucleation of the metal oxide to the formation of the thermodynamically stable oxide – represent a scientifically challenging and technologically important terra incognito. Furthermore, since environmental stability is an essential property of most engineered materials, many theories exist to explain its mechanisms. However, nearly all classical theories assume a uniform growing film, where structural changes are not considered because of the previous lack of experimental methods to visualize this non-uniform growth under conditions that allowed for highly controlled surfaces and impurities. One can now see structural changes under controlled surface conditions, by in situ ultra-high vacuum transmission electron microscopy (UHV-TEM), and thereby challenge the commonly used assumption of a uniform oxide formation. Here, we present a systematic study of the dynamics of the initial and transient oxidation stages of a metal and alloys with in situ UHV-TEM. We have previously demonstrated that the formation of epitaxial Cu2O 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, temperatures and composition. For Cu-Au oxidation, the oxidation mechanisms change due to the limited Cu around the oxide island leading to a dendritic growth of the Cu2O islands. For Cu-Ni oxidation, the addition of Ni causes the formation Cu2O and/or NiO where the oxide type(s) and the relative orientation with the film depend on the Ni concentration, oxygen partial pressure and temperature. This research program is funded by the National Science Foundation (DMR 0706171) and Department of Energy (DE-FG02-07ER46446).

Thursday Afternoon, October 23, 2008

In Situ Microscopy and Spectroscopy: Interfacial and Nanoscale Science Topical Conference
Room: 310 - Session IS+NC-ThA

In Situ Microscopy - Dynamic Nanoscale Processes
Moderator: D.J. Miller, Argonne National Laboratory

2:00pm **IS+NC-ThA1 In-situ Electromagnetic Field Experiments in the Analytical Electron Microscope**, ***N.J. Zaluzec***, *D.J. Miiller*, Argonne National Laboratory **INVITED**

The term in-situ microscopy has been traditionally used to describe studies of liquid/solid or gas/solid interactions. While this is an important aspect of materials characterization it represents only one regime of the study of materials under real-world environments. Recent work at the ANL EMCenter has focused upon dynamic studies of materials in the analytical electron microscope (AEM) using electromagnetic excitation and the observation and characterization using both imaging and spectroscopy. In magnetic and anti-ferromagnetic materials we drive transitions between states by means of externally applied fields and/or temperature and observe both qualitatively and quantitatively the changes which occur as a function of the driving transition. In the area of nanoscale materials we are investigating the use of in-situ optical excitation of novel structures and then performing simultaneous electron spectroscopy to elucidate the changes in their plasmonic features. Some aspects of this work have reached the routine level, while others particularly those requiring time synchronized excitation and observation are more demanding requiring significant modifications of conventional instrumentation.

2:40pm **IS+NC-ThA3 In-Situ Electron Microscopy Enabled by a TEM-SPM Platform**, ***J. Huang***, Sandia National Laboratories **INVITED**

Transmission electron microscopy (TEM) is a powerful tool for structural characterization of materials. However in-situ studies of the mechanical, electrical and thermal properties of materials at a nanometer scale are still challenging. A scanning probe microscopy (SPM), including scanning tunneling microscopy (STM), atomic force microscopy (AFM), and nano-indentor, explores the physical and mechanical properties of materials down to a single atom level but without internal structural information. A combined TEM-SPM platform, which integrates a fully functional SPM into a TEM, takes advantage of both the SPM and the TEM capabilities and provides unprecedented opportunities to probe the structural, mechanical, electrical, and thermal properties of materials in-situ down to a nanometer scale. This allows for direct correlation of the physical and mechanical properties to the atomic-scale microstructure. In this talk, I will review our recent progress in using the TEM-SPM platform to probe the electrical and mechanical properties of carbon nanotubes.[1] First, individual multiwall carbon nanotubes are peeled off layer-by-layer by electric breakdown inside the TEM. This provided new insights into the transport property of nanotubes. Second, plastic deformation, such as superplasticity, kink motion, dislocation climb, and vacancy migration, was discovered in nanotubes for the first time. Emerging directions of using the TEM-SPM platform to enable in-situ thermal/thermoelectric property measurements will be discussed.

[1] J.Y. Huang et al., Nature 439, 281 (2006); J.Y. Huang et al., Phys. Rev. Lett. 94, 236802 (2005); 97, 075501 (2006); 98, 185501 (2007); 99, 175593 (2007); 100, 035503 (2008).

3:20pm **IS+NC-ThA5 Investigating Sliding-induced Graphitization of Diamond-like Carbon Films by In Situ TEM**, ***A. M'ndange-Pfupfu***, *L.D. Marks,* Northwestern University*, O.L. Eryilmaz, A. Erdemir*, Argonne National Laboratory

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.[1] 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 precise mechanisms of graphitization seen in diamond-like carbon films.[2] 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.[3] By using electron energy loss spectroscopy combined with high resolution imaging, we can observe the changes in bonding that occur during graphitization as they happen. We study the results over a range of films with differing levels of hydrogenation.

[1] A P Merkle and L D Marks. "Friction in Full View." Applied Physics Letters 90, 064101 (2007).

[2] Y Liu, A Erdermir, and E I Meletis. "A study of the wear mechanism of diamond-like carbon films." Surface and Coatings Technology 82 (1996) 48-56.

[3] A V Sumant, et. al. "Surface chemistry and bonding configuration of ultrananocrystalline diamond surfaces and their effects on nanotribological properties." Physical Review B 76, 235429 (2007).

4:00pm **IS+NC-ThA7 Kinetics of Individual Nucleation Events during Nanoscale Vapor-Liquid-Solid Growth**, ***F.M. Ross***, IBM T. J. Watson Research Center **INVITED**

The growth of self-assembled nanostructures, such as nanowires, must be carried out with a high degree of control if electronic and optoelectronic devices are to be fabricated reliably. In particular, nucleation must be well controlled if a single nanostructure is to form at each location over a wafer. Using ultra high vacuum TEM, we have therefore examined nucleation in the model vapor-liquid-solid systems Si-Au and Ge-Au. We will present a quantitative analysis of both the initial transformation from solid Au to liquid Au-Si or Au-Ge eutectic and the subsequent formation of the nanowire nucleus. Quantitative measurements of nucleation and growth kinetics agree well with a simple model that provides a unified picture of the growth process. Nucleation is heterogeneous, occurring consistently at the edge of the liquid droplet, yet it is intrinsic and highly reproducible. We estimate the critical supersaturation required for nucleation, and find that size effects are surprisingly small, even for systems down to 12 nm in diameter. Nucleation is also important when forming nanowire heterostructures, and we examine this process in situ by observing the epitaxial nucleation of Si and Ge on wires formed of dissimilar materials such as GaP and GaAs. The observation and analysis of individual nucleation events in nanoscale systems leads to results that may be relevant to the formation of nanostructures for real-world applications.

4:40pm **IS+NC-ThA9 Atomic Resolution In-Situ Environmental Transmission Electron Microscopy on Nanostructures**, ***X.F. Zhang***, Hitachi High Technologies America, Inc.*, T. Kamino*, Hitachi High Technologies Corp., Japan **INVITED**

In recent years, progresses in in-situ transmission electron microscopy (TEM) pro-vided unique imaging and analytical capabilities for studying structural evolutions in versatile environments. Aiming at atomic resolution in-situ TEM capability, we have developed various sample holders including gas injection-heating holder, single- and double-tilt heating holders, and double-heater sample holder.[1-2] Using these sample holders, in-situ heating TEM studies in vacuum or in a gas envi-ronment, and in-situ evaporation deposition can be done in a standard Hitachi 300 kV H-9500 high-resolution transmission electron microscope,[3] true atomic resolution can be achieved at elevated temperatures for example at 1500oC, and digital recording of the dynamic structural evolutions is realized using a high speed CCD camera. Various nanomaterials have been studied at elevated temperatures with or without a gas environment. Effects of electron beam irradiation on nanomaterials were also evaluated. It has been found that 300 kV electron beam could alter some nanostructures at room temperature even though the nanomaterials were composed of 'robust' materials such as carbon and metals. However, when heating samples to elevated temperatures, electron beam irradiation helped in-situ TEM study in many ways that it might minimize knock-on damages, burn off amorphous surface layers, or trigger structural changes in nanostructures. In study of metallic nanoparticles, atomic layer-by-atomic layer structural changes at various temperatures have been observed directly, the changes in structure would be impossible to be explained without the in-situ atomic resolution TEM. Structural changes in oxide nanoparticles were observed at high temperatures and the atomic resolution TEM helped to understand the phase transformation process. These data provide insights into the structural processes in the middle stage before the environmental impacts became catastrophic to materials, therefore can help to elucidate puzzled phenomena often encountered in ex-situ experiments or in in-situ TEM experiments at low resolution or with too long time intervals for image recording.

[1] T. Kamino and H. Saka, Microsc. Microanal. Microstruct. 4 (1993) p. 127.

[2] T. Kamino, T. Yaguchi, M. Konno, A. Watabe, T. Marukawa, T. Mima, K. Kuroda, H. Saka, S. Arai, H. Makino, Y. Suzuki and K. Kishita, J. of Electron Microscopy 54 (2005) p. 497.

[3] X.F. Zhang and T. Kamino, Microscopy Today 9 (2006) p. 16.

5:20pm **IS+NC-ThA11 In-Situ Transmission Electron Microscopy Studies of Chemical and Thermal Stabilities of Carbon-Coated Titania Nanoparticles**, *M. Pozuelo,* University of California, Los Angeles, *X.F. Zhang,* Hitachi High Technologies America, Inc., *J.H. Park,* University of California Los Angeles, *R. Koc,* Southern Illinois University at Carbondale, ***S. Kodambaka***, University of California, Los Angeles

Transition-metal carbides such as titanium carbide (TiC) form a technologically-important class of materials with applications in a wide variety of areas including catalysis, energy storage, high-temperature corrosion- and oxidation-resistant coatings, and as structural composites. For all these applications, high surface area, small size, and phase-pure particles are desirable. One of the common methods for TiC production is carbothermal reduction of TiO_2 at elevated temperatures (>1200 °C). This reduction reaction is suggested to occur via successive formation of lower oxides of titanium along with the emission of CO and CO_2 gases. However, the exact details of the reaction kinetics, which control the final particle size, shape, and crystal structure are largely unknown. As a first step toward the development of a fundamental understanding of the carbothermal reduction process we chose carbon-coated TiO_2 particles as a model system. Using in situ lattice-resolution transmission electron microscopy (TEM), we study the chemical and thermal stabilities of individual C-coated titania (TiO_2) nanoparticles during annealing in vacuum at temperatures up to 1000 oC. First, C-coated titania particles are prepared by pyrolysis of propylene (C_3H_6) gas in an oxygen-free environment at ~ 600 °C in a tube furnace filled with titania powders (average size ~ 20 nm). This process resulted in a uniform coating of pyrolytic carbon shell (thickness ~2-5 nm) around individual oxide particles. In situ TEM experiments are carried out at Hitachi EM Lab in Pleasanton, California using an atomic resolution Hitachi H-9500 300 kV TEM (base pressure ~ $10^{-6}6$ Torr) which allows in-situ heating in vacuum or in a gas environment. The oxide-core/C-shell nanoparticles are deposited directly onto a heating filament of the gas injection-heating TEM sample holder. Lattice-resolution TEM images are acquired at video rate (15 frames/s) while heating the particles in vacuum for times up to 5 h. Energy dispersive X-ray spectra (EDX) are obtained at room temperature from the samples before and after the annealing experiments. We find several interesting phenomena: 1) crystallization of carbon to form graphene layers preferentially on the lowest-energy planes of TiO_2; 2) shrinking and eventual disappearance of the oxide cores while being encapsulated by carbon, resulting in the formation of hollow-core graphene shell structures; 3) reduction of TiO_2 to lower oxides. These studies provide atomic-scale insights into the early stage carbothermal reduction process leading to the synthesis of TiC particles.

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