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 / a-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-depostied 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 informaiton 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 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 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 ~300°C but Cu2O and NiO show limited miscibility. Nickel oxide, which has the cubic NaCl crystal structure, has a more negative standard free energy of formation than Cu2O, which is simple cubic, and is expected to form more readily. In this case, depending on the environmental pO2, 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 Cu2O 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-Angstrom 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.[1] These holders can be used to study transport phenomena across interfaces, sintering phenomena in nanoparticles, and elevated temperature studies of catalysts.[2,3]

[1] J. Damiano, D.P. Nackashi and S.E. Mick; Microsc Microanal 14(Suppl 2) 1332, 2008.

[2] M. Briceno, et al., Microsc Microanal 14(Suppl 2) 1336, 2008.

[3] 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 superllatices. I will illustrate the resolution of the aberration corrected electron microscopy and EELS, and what we have leant 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 Å, 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.

References

[1] R. Sharma and K. Weiss, Microscopy Research and Technique **42**(4) (1998), p. 270-280.

[2] P.L. Hansen, J.B. Wagner, S. Helveg, J.R. Rostrup-Nielsen, B.S. Clausen and Topsoe, H., Science **295**(5562) (2002) p. 2053-2055.

[3] S. Helveg, C. Lopez-Cartes, J. Sehested, P.L. Hansen, B.S. Clausen, J.R. Rostrup-Nielsen, F. Abild-Pedersen and Norskov, J.K., Nature **427** (2004) p. 426-429.

[4] R. Sharma, P. Rez, M. Brown, G.H. Du, and M.M.J. Treacy, Nanotechnology **18**(12) (2007)

[5] S. Hofmann, R. Sharma, C. Ducati, G. Du, C. Mattevi, C. Cepek, M. Cantoro, S. Pisana, A. Parvez, F. Cervantes-Sodi, A.C. Ferrari, R. Dunin-Borkowski, S. Lizzit, L. Petaccia, A. Goldoni and J. Robertson, Nano Letters **7**(3) (2007) p. 602-608.

[6] P.L. Gai, R. Sharma and F.M. Ross, MRS Bulletin **33**(2) (2008) p. 107-114.

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 (MoS2). 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 MoS2, 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 that takes place at the interface.

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