

Wednesday Morning, October 20, 2010

In Situ Microscopy and Spectroscopy Topical Conference

Room: Acoma - Session IS+AS+NS+MI-WeM

In Situ Microscopy/Spectroscopy – In Situ Nanoscale Processes

Moderator: A. Mkhoyan, University of Minnesota

8:00am **IS+AS+NS+MI-WeM1 Low-dimensional Superconductivity of Pb Nanostructures**, J. Kim, H. Nam, G.A. Fiete, C.K. Shih, The University of Texas at Austin

The influence of low-dimensional geometries on superconductivity is an important issue to study because in low dimensions it is key to understanding coherence and robustness of the superconducting state in quantum-mechanically confined geometries. The lateral size dependence of superconductivity on 2 dimensional Pb islands is studied by using *in-situ* low temperature Scanning Tunneling Microscopy/Spectroscopy (STM/S). The superconducting transition temperature (T_c) of each island is obtained by fitting the STS data with a BCS-like density of states. It is found that superconductivity shows a clear dependence on the Pb island lateral size even when it is larger than the bulk coherence length (~80nm), and it is also found that T_c drops very quickly below a certain lateral size. In addition, an intriguing lateral proximity effect is observed at the interface of different local superconducting regions of Pb islands. Current imaging tunneling spectroscopy (CITS) is used to visualize this proximity effect in real space.

8:20am **IS+AS+NS+MI-WeM2 Enabling the Measurement of In-Situ, Site-Specific Mineral Transformation Rates in Supercritical CO₂ through Development of a High Pressure AFM**, S. Lea, Pacific Northwest National Laboratory, S.R. Higgins, Wright State University, K.G. Knauss, Lawrence Berkeley National Laboratory, K.M. Rosso, Pacific Northwest National Laboratory

Capture and storage of carbon dioxide in deep geologic formations represents one promising scenario for minimizing the impacts of greenhouse gases on global warming. At issue is the ability to demonstrate that CO₂ will remain stored in the geological formation over the long-term and so knowledge of mineral-fluid transformation rates is critical for this determination. The majority of previous research on mineral-fluid interactions has focused primarily on the reactivity of minerals in aqueous solutions containing CO₂. However, caprock integrity would be dictated primarily by mineral interaction with supercritical CO₂ (scCO₂) as the buoyant phase slowly displaces or desiccates residual aqueous solution at these surfaces. Many of the mechanisms of mineral interfacial reactions with hydrated or water-saturated CO₂ are unknown and there are unique challenges to obtain kinetic and thermodynamic data for mineral transformation reactions in these fluids.

A high-pressure atomic force microscope (AFM) is currently under development that will enable *in-situ* site-specific measurements of metal carbonate nucleation and growth rates on mineral surfaces in contact with scCO₂ fluids. This apparatus is based on the hydrothermal AFM that was developed by Higgins et al.¹, but includes some enhancements and is designed to handle pressures up to 1500 psi. The noise in our optically-based cantilever deflection detection scheme is subject to perturbations in the density (and therefore index of refraction) of the compressible supercritical fluid. Consequently, variations in temperature and pressure within the fluid cell can have a significant impact in our ability to discern atomic steps on mineral surfaces. We demonstrate with our test fluid cell that the equivalent rms noise in the deflection signal is similar to (and in some cases less than) the equivalent noise for an AFM in its 'standard configuration' under controlled pressures of ~80 bar and temperatures of 60-80 °C and therefore *in-situ* atomic scale imaging of mineral surfaces in scCO₂ should be possible. This talk will also focus on recent progress in the development of this instrumentation, which will enable a unique platform for elucidating the role of water in mineral transformations, providing a means for determining effective kinetic constants.

1. Higgins, S. R.; Eggleston, C. M.; Knauss, K. G.; Boro, C. O., A hydrothermal atomic force microscope for imaging in aqueous solution up to 150°C. *Review of Scientific Instruments* **1998**, 69 (8), 2994-2998.

8:40am **IS+AS+NS+MI-WeM3 Au on VLS-grown Si Nanowires: Spreading of the Liquid Metal Seed**, E. Dailey, P. Madras, J. Drucker, Arizona State University **INVITED**

In situ TEM shows that liquid AuSi spreads from the seed along the NW sidewalls to form a thin liquid sheath for some growth conditions. The thin

liquid film phase separates to form small solid Au clusters when the NW is cooled below the solidus temperature. Quantitative composition maps show that the Au composition is highest near the NW tip. The thickness and length that the liquid film spreads from the seed is growth condition and NW diameter dependent and represents a steady state during growth. These observations can be related to the spreading thermodynamics of liquid droplets along cylinders. Growth conditions for which the liquid AuSi spreads from the seed stabilize 'vertical' growth along <111> by lowering the surface energy of the high-energy {112} bounding facets. In contrast, the NWs kink toward <112> when grown using conditions that favor growth with Au-free sidewalls since these NWs are bound by facets that are found on the Si equilibrium crystal shape.

9:20am **IS+AS+NS+MI-WeM5 Advanced Study of Nanoscale Mechanisms: Plans for In-Situ TEM Microreactor, Gas Cell, and Multi-Beam Irradiation Experiments**, B.G. Clark, K. Hattar, Sandia National Laboratories, D. Nackashi, J. Damiano, S. Mick, Protochips, Inc., B.L. Doyle, Sandia National Laboratories

Over the years, in-situ TEM experiments have allowed for observation of material mechanisms at high resolution and in real time; a feat often not possible with any other experimental technique. With increasing demand for understanding nanoscale material mechanisms, both with growth in the applications of nanomaterials and in the development of predictive materials models based on experimental observation, the realm of in-situ TEM experiments has continued to expand. Highlighted in this presentation will be the development of three, exciting new capabilities for in-situ TEM experiments at Sandia National Labs.

The first part of the talk will focus on the development of two new in-situ TEM stages. Expanding on the success of static and single inlet-outlet liquid cells, we are designing a new in-situ TEM microreactor liquid cell with the capability to mix fluids in controlled temperature regimes, to view reactions as a function of time, and to capture and analyze reaction products. Research programs using this stage will pursue studies of self-assembly, directed assembly, and nanoparticle formation and growth. In addition, for observation of advanced degradation of materials in the presence of gases and/or vapor, a new in-situ TEM gas cell stage is being developed. This stage will have the capability to study a variety of gas-solid and vapor-solid interactions, such as corrosion, oxidation, and hydriding, with accurate control over temperature and pressure. Envisioned research will include understanding environmental degradation of materials during storage of spent nuclear fuels, an issue of critical importance for the future of nuclear energy.

The second part of the talk will highlight the development of a new, triple-ion-beam in-situ irradiation TEM. By combining expertise in in-situ TEM experiments with expertise in ion beam studies, planning is currently underway that would culminate in the construction of an instrument capable of studying the effects of bombardment by up to three ion beams simultaneously within the TEM. This unique, triple-ion-beam capability would enable advanced experiments such as real-time studies of neutron induced damage and transmutation in a fission/fusion reactor by combining Fe, He, and H ions.

*This work is supported by the Division of Materials Science and Engineering, Office of Basic Energy Sciences, U.S. Department of Energy. Sandia National Laboratories is a multi-program laboratory operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin company, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

9:40am **IS+AS+NS+MI-WeM6 In Situ TEM Investigation into the Thermal Stability of Nanograined FCC Metals and Alloys**, K. Hattar, B.G. Clark, Sandia National Laboratories, J. Kacher, University of Illinois at Urbana-Champaign, J.A. Knapp, D.M. Follstaedt, L.N. Brewer, Sandia National Laboratories, I.M. Robertson, University of Illinois at Urbana-Champaign

Nanostructured materials often display very unique properties related to their far-from-equilibrium nature. Due to these unique structures, many of these materials transform into other, more stable microstructures with minimal thermal excitation. This work will highlight examples of the unexpected routes taken during the microstructural evolution of pulsed-laser deposited (PLD) free-standing face-centered cubic (FCC) thin films as a function of deposition condition and annealing temperatures. A direct comparison between the grain growth dynamics observed during *in situ* TEM annealing experiments in PLD films of high-purity aluminum, copper, gold and nickel films, as well as aluminum-alumina alloys shows a multitude of kinetics. For high-purity systems film thickness, void density, grain size distribution, and deposition temperature were found to be the

primary factors observed controlling the rate, extent, and nature of the grain growth. The growth dynamics ranged from nearly classical normal grain growth to abnormal grain growth resulting in a bimodal grain size distribution. The grain growth rate was found to be highly dependent on the materials system despite all of the films being nanograined FCC metals produced by similar PLD parameters. The investigation of the aluminum-alumina alloys produced under various compositions and deposition parameters suggests that particle pinning can be used to maintain nanostructured films, even after annealing treatments at high homologous temperatures.

In addition to investigating the grain growth dynamics and the resulting grain size distribution, the variety of internal microstructures formed from thermal annealing were evaluated. These structures ranged from intergranular voids to stacking-fault tetrahedra. An unexpected, metastable hexagonal-closed packed phase was indentified in the high-purity nickel films. These *in situ* TEM observations have provided key insight into the microstructural evolution of nanograined free-standing metal films and the defect structure present in the grains resulting from various growth dynamics, in addition to suggesting multiple methods to tailor the structure and the resulting properties of nanostructured free-standing films.

*This work is supported by the Division of Materials Science and Engineering, Office of Basic Energy Sciences, U.S. Department of Energy both at Sandia and under grant DE-FG02-07ER46443. Sandia National Laboratories is a multi-program laboratory operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin company, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

10:40am **IS+AS+NS+MI-WeM9 In Situ TEM Studies of Nanomagnetism and Thermal Transport, J. Cumings, University of Maryland**

INVITED

The transmission electron microscope is a powerful tool for many areas of nanoscience. The combination of high spatial resolution and high time resolution, giving video-rate imaging, makes it uniquely capable of many types of studies of phenomena in-situ during imaging. Here I will present two areas where we have made recent advances. In nanomagnetic structures, it is possible to image in real-time the reversal process of coupled systems called artificial spin ice. These systems exhibit frustration, leaving disorder in their lowest energy magnetic configurations. I will present studies showing the magnetic reversal processes for these structures, revealing that microscopically correlated events lead to avalanche phenomena. A second topic that I will present is electron thermal microscopy of carbon nanotubes. Here, a new technique will be introduced that allows thermal imaging with nanoscale spatial resolution. This technique has been used to study the thermal transport through carbon nanotubes, and I will present results showing that thermal contact resistance can limit the thermal transport in nanotubes. I will show that this contact resistance can be tuned by two orders of magnitude by appropriately controlling the fabrication of the contacts. Together these results serve to demonstrate the capabilities of studies utilizing in-situ transmission electron microscopy.

11:20am **IS+AS+NS+MI-WeM11 In-situ Infrared Transmission Analysis of Atomic Layer Deposition Reactions on Polymer Films and Fibers, G.N. Parsons, B. Gong, J.S. Jur, C. Oldham, K. Lee, North Carolina State University**

Many new product applications related to packaging, filtration, protection and others offer substantial opportunities and raise new demands for polymer/inorganic thin film integration and surface modification. In-situ transmission infrared spectroscopy can provide critical insight into reaction mechanisms that proceed during inorganic film deposition on organics. We are particularly interested in low-temperature atomic layer deposition (ALD) which ideally proceeds through a binary sequence of self-limiting surface reactions to form highly conformal and uniform films on high surface area structures. In-situ IR spectroscopy allows us to probe and identify specific polymer/precursor reaction mechanisms that occur during precursor and reactant exposure. Typical atomic layer deposition precursors and reactants include trimethylaluminum (TMA), diethyl zinc (DEZ) and water, and polymer materials studied to date include polypropylene, polyamide-6, polyesters (such as polybutylene terephthalate), cellulose, polyvinyl alcohol and others. We have investigated deposition reactions on planar polymer sheets as well as micro- and nano-scale polymer fibers.

In-situ IR transmission data demonstrates that typical non-reactive materials such as polypropylene will take up precursors with minimal precursor/polymer reaction, resulting in subsurface alumina nucleation. Polymers with more reactive backbone or side chain groups, such as cellulose, polyvinyl alcohol or polyamide-6 react readily with the precursor. For example, when polyamide-6 is exposed to TMA, N-H and C-O stretching modes decrease markedly, indicating that TMA attacks the

electrophilic carbon atom in the carbonyl group leading to methyl insertion and formation of C-O-Al- and C-CH₃ bonds. Electron micrograph images of polyamide fibers after TMA exposure confirms significant extent of reaction. Deposition on cellulose cotton fibers, however, shows primarily surface adsorption, resulting in true ALD growth and highly conformal film coatings by TEM. We will show details of the in-situ transmission ALD reactor, and illustrate how the tool is especially amenable and adaptable to in-situ surface reaction analysis on polymer fiber networks.

Authors Index

Bold page numbers indicate the presenter

— B —

Brewer, L.N.: IS+AS+NS+MI-WeM6, 1

— C —

Clark, B.G.: IS+AS+NS+MI-WeM5, **1**;
IS+AS+NS+MI-WeM6, 1

Cumings, J.: IS+AS+NS+MI-WeM9, **2**

— D —

Dailey, E.: IS+AS+NS+MI-WeM3, 1

Damiano, J.: IS+AS+NS+MI-WeM5, 1

Doyle, B.L.: IS+AS+NS+MI-WeM5, 1

Drucker, J.: IS+AS+NS+MI-WeM3, **1**

— F —

Fiete, G.A.: IS+AS+NS+MI-WeM1, 1

Follstaedt, D.M.: IS+AS+NS+MI-WeM6, 1

— G —

Gong, B.: IS+AS+NS+MI-WeM11, 2

— H —

Hattar, K.: IS+AS+NS+MI-WeM5, 1;
IS+AS+NS+MI-WeM6, **1**

Higgins, S.R.: IS+AS+NS+MI-WeM2, 1

— J —

Jur, J.S.: IS+AS+NS+MI-WeM11, 2

— K —

Kacher, J.: IS+AS+NS+MI-WeM6, 1

Kim, J.: IS+AS+NS+MI-WeM1, **1**

Knapp, J.A.: IS+AS+NS+MI-WeM6, 1

Knauss, K.G.: IS+AS+NS+MI-WeM2, 1

— L —

Lea, S.: IS+AS+NS+MI-WeM2, **1**

Lee, K.: IS+AS+NS+MI-WeM11, 2

— M —

Madras, P.: IS+AS+NS+MI-WeM3, 1

Mick, S.: IS+AS+NS+MI-WeM5, 1

— N —

Nackashi, D.: IS+AS+NS+MI-WeM5, 1

Nam, H.: IS+AS+NS+MI-WeM1, 1

— O —

Oldham, C.: IS+AS+NS+MI-WeM11, 2

— P —

Parsons, G.N.: IS+AS+NS+MI-WeM11, **2**

— R —

Robertson, I.M.: IS+AS+NS+MI-WeM6, 1

Rosso, K.M.: IS+AS+NS+MI-WeM2, 1

— S —

Shih, C.K.: IS+AS+NS+MI-WeM1, 1