Monday Morning, October 15, 2007

In-situ Electron Microscopy Topical Conference

Room: 618 - Session IE-MoM

Structure-Property Characterization

Moderator: S. Kodambaka, University of California, Los Angeles

8:00am **IE-MoM1 The TEAM Project and its Potential for In-Situ Experimentation**, ***U. Dahmen***, Lawrence Berkeley National Laboratory **INVITED**

Advanced electron microscopes give us unprecedented views of materials and their unusual behavior on the nanoscale. It is possible to observe how a nanocrystal grows or melts or changes its structure atom by atom, or to investigate the structure of nanocrystals embedded in microcrystals. However, until now, electron microscopes have remained limited by lens aberrations. As it becomes possible to overcome this limitation with aberration correcting optics, a broad range of new possibilities for research and discovery by high resolution imaging opens up. The improved instrument resolution, contrast and sensitivity create the opportunity to directly observe the atomic-scale order, electronic structure, and dynamics of individual nanoscale structures. To take advantage of this opportunity, the TEAM project (Transmission Electron Aberration-corrected Microscope) brings together several microscopy groups in a collaborative effort to jointly design and construct a new generation microscope with extraordinary capabilities. Led by the National Center for Electron Microscopy, the project involves several Department of Energy research efforts and commercial partners. After its completion in 2009, the instrument will be made available to the scientific user community at the National Center for Electron Microscopy. The vision for the TEAM project is the idea of providing a sample space for electron scattering experiments in a tunable electron optical environment by removing some of the constraints that have limited electron microscopy until now. The resulting improvements in spatial, spectral and temporal resolution, the increased space around the sample, and the possibility of exotic electron-optical settings will enable new types of experiments. The TEAM microscope will feature unique corrector elements for spherical and chromatic aberrations, a novel AFM-inspired specimen stage, a high-brightness gun and numerous other innovations that will extend resolution down to the half-Angstrom level. The most important scientific driving force that emerged from a series of workshops is the need for in-situ experiments to observe directly the relationship between structure and properties of individual nanoscale objects. Successive instruments built on the TEAM platform would provide unique experimental capabilities to probe dynamics and mechanisms of reactions such as catalysis in a gaseous environment, or the effects of gradients in temperature, composition, stress, magnetic or electric fields. This talk will highlight some recent discoveries in nanoscale materials science using high resolution electron microscopy and outline some research opportunities for future users of TEAM instrument.

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8:40am **IE-MoM3 Dynamic Studies of Magnetization Reversal Processes and Future Prospects for In-Situ TEM**, ***B. Kabius***, *A.K. Petford-Long*, Argonne National Laboratory **INVITED**

The rapid increase in information storage density, memory density and speed have been brought about in part by the development of new materials, often consisting of layered structures, with properties that are engineered by controlling the microstructure and chemical profile. The layer thicknesses are of the order of a few nanometers, and the deposition techniques used tend to give polycrystalline films, resulting in variations in properties across the structures. One of the most spectacular examples is the development of devices based on the giant magnetoresistance (GMR) phenomenon, such as the spin-valve and the spin-dependent tunneling junction used for read heads or magnetoresistive random access memories. In addition, patterned single layer structures are of importance for both media and memory applications. The behavior of these materials relies on the local magnetic domain structure and magnetization reversal mechanism, and one of the techniques enabling micromagnetic studies at the sub-micron scale is Lorentz transmission electron microscopy (LTEM) which allows the magnetic domain structure and magnetization reversal mechanism of a FM material to be investigated dynamically in real-time with a resolution of a few nm. We have used LTEM and in-situ magnetizing experiments to study magnetization reversal in a range of materials including spin-tunnel junctions and patterned thin film elements. Quantitative analysis of the Lorentz TEM data has been carried out using the transport of intensity equation (TIE) approach. Studies of active spin valves have shown the way in which the magnetization reversal process depends on applied current. In addition to the local variations in the magnetic properties induced by the microstructure of the films, further variations arise when the films are patterned to form small elements and results will be presented for a range of structures patterned both from single layers and from device structures. Results of further in situ experiments to measure the local tunneling properties of magnetic tunnel junctions will also be presented. Recent progress in electron beam instrumentation is expected to have a strong impact on in-situ TEM, especially LTEM. E.g., correction of chromatic aberration is at present under development within the frame work of the TEAM project. The benefits of this novel corrector for in-situ experiments will be discussed.

9:20am **IE-MoM5 Understanding Dislocation Dynamics and the link to Macroscopic Properties**, ***I.M. Robertson***, *G. Liu, B. Clark, B. Miller*, University of Illinois **INVITED**

The behaviour of dislocations under an applied load and their interaction with obstacles, such as grain boundaries, precipitates, voids etc., can be revealed be conducting deformation experiments in real time in situ in the transmission electron microscope. Linking the insight gained form such studies to macroscopic measurements of property changes remains challenging but significant progress has been made. It will be shown that grain and twin boundaries serve as sources and sinks for, and barriers to perfect and partial dislocations. From information learned from these studies, criteria for the transfer of slip across grain boundaries and interfaces have been established. However, the microstructure is not static and evolves with increasing strain. For example, the process of slip transmission can result in the destruction of the grain boundary locally and this influences subsequent deformation activity. These observations provided a basis for developing strategies for incorporating grain boundary effects in large-scale predictive models of mechanical behaviour. Studies of the interaction of dislocations with precipitates with different interfacial character as a function of temperature have revealed a rich variety of complex dislocation-precipitate interactions and by-pass mechanisms. The interaction type depends on the particle coherency and size, the nature and Burgers vector of the dislocation, the geometry of the interaction, the number of interactions, and the test temperature. It is also possible and common for multiple slip systems to interact with the particle consecutively or simultaneously and this changes the nature of the interactions. The number and complexity of the interactions and the richness of the possibilities have significant implications for current models of mechanical properties of precipitate-hardened systems. This paper emphasizes what can be learned from conducting dynamic experiments in the electron microscope and how such insights can and are being used as a basis for formulating physically-based constitutive relationships to predict macroscopic mechanical properties of thin and thick films.

10:20am **IE-MoM8 Structure and Structural Transitions of Supported Nanoparticles and In-Situ RHEED Observations**, *K. Sato, W.J. Huang*, ***J.M. Zuo***, University of Illinois, Urbana-Champaign **INVITED**

Understanding different structures of nanoparticles and their transition can have a large impact on our ability to self-assemble controlled nanostructures and understanding properties of nanoparticles. Small nanoparticles of a few nanometers in diameter are difficult to characterize by traditional surface characterization techniques. Here we report two recent developments in nanoparticle characterization. The first is an in-situ RHEED characterization of the size dependence of structural transition from multiply-twinned particle (MTP) to epitaxial face centered cubic (FCC) nanocrystal for Ag nanoparticle formed on Si(001) surfaces. The transition from MTP to nanocrystals was promoted by post-deposition annealing. Clear particle size dependence is found in the epitaxial formation temperatures (T_E), which is about 2/3 of the calculated, size-dependent, melting temperature (T_M) for particles larger than 2 nm in diameter. For smaller nanoparticles, T_E is about the same as T_M. Once nanocrystals are formed, they decay and disappear in a narrow temperature range between 794 and 849 K. No evidence of nanocrystal melting was detected from the RHEED observation. In the second study, we show that coherent electron diffraction patterns recorded from individual nanocrystals are very sensitive to, and can be used to study, the structures of nanocrystal surfaces. We use this to study the bond-length dependent atomic contractions in Au nanocrystals 3 to 5 nm. Evidences of inhomogeneous surface relaxation will be presented.

11:00am **IE-MoM10 In-Situ Hot-Stage TEM of Interface Dynamics and Phase Transformations in Materials**, ***J.M. Howe***, *A.R.S. Gautam*, *S.K. Eswaramoorthy*, University of Virginia **INVITED**

In-situ transmission electron microscopy (TEM) is an indispensable tool for determining the behavior of materials and interfaces under actual experimental conditions. This paper focuses on the results from in-situ heating experiments performed on nanoparticles in the TEM, using either high-resolution TEM (HRTEM) imaging or energy-dispersive X-ray spectroscopy (EDXS). Three different types of transformations and the fundamental processes associated with them are discussed. These include the atomic-level dynamics of an order-disorder interface near equilibrium in a Au-Cu alloy nanoparticle, the mechanisms of migration and coalescence of Au-Cu alloy nanoparticles supported on an amorphous-C thin-film, and the nucleation and growth behavior of phases and how elements partition between them in partially molten Al-Cu-Mg-Si nanoparticles in near-equilibrium and highly undercooled conditions. Some of the major results from these studies are summarized as follows. For the order-disorder interface near equilibrium in a Au-Cu alloy nanoparticle, it was found that both the interphase boundary position and thickness fluctuate with time and that the behavior of the disordered side of the interphase boundary differs from that of the ordered side. These features can be explained in terms of the physical properties of the different phases and the energetics of the interphase boundary. In the case of two Au-Cu alloy nanoparticles supported on an amorphous-C thin-film, it was found that Ostwald ripening and particle motion occur simultaneously, through collective surface fluctuations and a directed diffusional flux between the two particles. This flux becomes directly visible during coalescence, where redistribution of mass on the large particle is also revealed. In the partially molten Al-Si-Cu-Mg alloy nanoparticle, it was found that the solid Al phase is completely wet by the liquid and therefore cannot nucleate heterogeneously on the Si phase or oxide surface. Because heterogeneous nucleation is eliminated, it was possible to directly determine the metastable liquidus and solidus phase boundaries in the undercooled liquid by EDXS, in addition to the compositions across the solid Si-liquid interface. This research was supported by NSF under Grants DMR-9908855 and DMR-0554792.

11:40am **IE-MoM12 Design and Development of an Environmental Cell for Dynamic In Situ Observation of Gas Solid Reactions at Elevated Temperatures**, ***P.V. Deshmukh***, *P.E. Fischione*, *C.M. Thomas*, *J.J. Gronsky*, E.A. Fischione Instruments, Inc.

In situ monitoring of events in transmission electron microscopy provides information on how materials behave in their true state in the presence of various gases, under varying conditions of temperature and pressure. These results are usually different from static, post-reaction observations.[1, 2,3] To facilitate applications that demand in situ observations, a transmission electron microscope specimen holder has been developed. This holder incorporates a gas flow and heating mechanism along with a window-type environmental cell. A controlled mixture of up to four different gases can be circulated through the cell. The specimen can be heated up to a temperature of 800 °C using a carbon dioxide laser. This heating technique provides major advantages over conventional heating methods in terms of product life, specimen heating time and design size. The cell design incorporates a 200 micron high chamber enclosed between a pair of 20 nm thick silicon nitride windows. The chamber can accommodate a specimen or a grid having a diameter of 3 mm and thickness in the range of 50 to 100 microns. The volume for the gas environment within the chamber is approximately 0.7 mm^3 and the gas path length is less than 0.1 mm. This holder has been designed by incorporating cutting edge heating and MEMS technology to achieve excellent resolution along with a low thermal drift. Successful application of this holder would provide scientists with an economical alternative to dedicated transmission electron microscopes for a vast array of in situ applications including understanding the basic material properties, catalysis reactions, semiconductor device development, and nano structure fabrication.

[1] Dynamic in situ electron microscopy as a tool to meet the challenges of the nanoworld, NSF workshop report, Tempe, Arizona, 2006.

[2] R. Sharma, Design and Application of Environmental Cell Transmission Electron Microscope for In Situ Observation of Gas Solid Reactions, Microscopy and Microanalysis, 7, 494, 2001.

[3] I M. Robertson and D. Teter, Controlled Environmental Transmission Electron Microscopy, Microscopy Research and Technique, 42, 260, 1998.

In-situ Electron Microscopy Topical Conference

Room: 618 - Session IE-MoA

Dynamics of Nanostructures

Moderator: D.J. Miller, Argonne National Laboratory

2:00pm **IE-MoA1 In-situ Environmental TEM of the Nucleation and Growth of One-Dimensional Nanostructures**, ***S. Takeda***, *H. Yoshida*, Osaka University and CREST-JST, Japan, *Y. Homma*, Tokyo University of Science and CREST-JST, Japan **INVITED**

Solid-gas reaction is a fundamental process of the synthesis of various nanomaterials. For example, carbon nanotubes (CNTs), one of the most promising nanomaterials for future nanotechnology, are grown from metal catalysts in gases containing carbon. In order to apply nanomaterials to future nanodevices, their growth mechanism needs to be better understood at the atomic level. In this respect, transmission electron microscopy (TEM) equipped with an environmental cell (E-cell), which is occasionally called environmental-TEM (ETEM), is one of the best techniques. We have examined the importance of ETEM for the study of the growth mechanism of CNTs via computer simulation of high resolution ETEM images of CNTs under an actual growth condition.[1] Moreover, several pioneer works have revealed various solid-gas reactions by ETEM. In this work, the growth process of CNTs has been actually observed by a newly designed ETEM (FEI Tecnai F20 equipped with E-cell) which has an information limit of nearly 0.15 nm even in 10 mbar N_2 gas. CNTs were grown by catalytic chemical vapor deposition (CVD) of methane, acetylene and so on. The metal catalysts, such as Co and Ni were deposited on a silicon substrate with surface oxide. In our CVD process, the pressure of gases ranges from 1 to 10^3 Pa and the temperature is set at 600 to 800°C. We investigate the growth mechanism and dynamics of CNTs via in situ observations of both catalyst nanoparticles and CNTs. As an example, we have succeeded in the observation of the growth of a short multi-walled CNT (MWNT). During the growth of the MWNT, the shape of the catalyst changes drastically. Before the growth, the shape of the catalyst is a sphere. Then, the shape changes into an elongated shape. At a certain moment, the catalyst lifts off the substrate and contracts to a spherical shape. At the same time, a MWNT grows. The details including other in situ observations of CNT growth will be presented at the meeting.

[1] H. Yoshida and S. Takeda, Phys. Rev. B 72, 195428 (2005).

2:40pm **IE-MoA3 Observation of Dynamic Nanoscale Processes Using Environmental Scanning Transmission Electron Microscope**, ***R. Sharma***, Arizona State University **INVITED**

The world of nanomaterials has become the 'real world' for most of the applications in the area of nanotechnology. As post-synthesis handling of materials at a nanoscale is not practical, nanomaterials often need to be synthesized directly as part of a device or circuit. This demand posted by nanotechnology has led to the modifications in the design of transmission electron microscopes that permit us to perform in situ synthesis and characterization simultaneously. In situ observations of the synthesis process are used to understand and evaluate the effect of synthesis conditions (starting material (reactants), temperature and pressure) on the morphology, structure and chemistry of the product. Moreover, functioning (e.g. activity of a catalyst) of many nanosystems changes during operation. The effect of operating condition (time, temperature, and the ambient) can be elucidated by atomic scale in situ observation. Such in situ observations can be used to optimize the synthesis conditions for nanomaterials with desired structure and properties and improve the functioning of nano systems. Environmental scanning transmission electron microscope (ESTEM) permits us to observe gas-solid interactions at elevated temperatures in gaseous environment. 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 chemical processes at nanometer level. Its applications range from in situ characterization of reaction steps such as oxidation-reduction or corrosion, to in situ synthesis of nanomaterials such as quantum dots, carbon nanotubes or Si nanowires. Examples including synthesis and characterization (e.g. CNT, Si nanowires) and structural modifications during functioning of nanomaterials (catalyst) will be used elucidate the applications of the ESTEM. Future applications and improvements in the instrument design will be discussed.

3:40pm **IE-MoA6 Using Real Time Electron Microscopy to Understand Nucleation and Growth in Semiconducting Nanowires and Carbon Nanotubes**, ***E.A. Stach***, *B.-J. Kim, S.-M. Kim, D.M. Zakharov*, Purdue University, *F.M. Ross, J. Tersoff*, IBM T.J. Watson Research Center, *S. Kodambaka*, UCLA, *M.C. Reuter, K. Reuter*, IBM T.J. Watson Research Center, *B. Maruyama, M. Pender*, Wright Patterson Air Force Research Laboratory **INVITED**

Semiconducting nanowires and carbon nanotubes are two of the primary 'new' materials of interest in the field of nanotechnology, This is because their small dimensions and unusual structures allow for new technologies to be established that exploit their unique electronic properties. We have been focused on understanding the mechanisms and kinetics associated with their nucleation and growth, in an attempt to provide a scientific framework for controlling their structure. Through the use of in-situ chemical vapor deposition in both ultra-high vacuum and at elevated pressures, we can observe the mechanisms of nucleation and quantitatively characterize the kinetics of these processes. In the case of vapor-liquid-solid silicon nanowire growth, we have found that the dissociative desorption of disilane is the rate limiting step. Additionally, after nucleation, we find that the nuclei undergo a rapid growth in size, driven by the supersaturation of silicon in the host gold-silicon liquid alloy drop. We will present a theoretical framework to describe this behavior which balances the roles of supersaturation, pressure and interface energies and show how this can be used to find the kinetic liquidus line in the AuSi phase diagram. In the case of carbon nanotube growth, we utilize a unique catalyst approach wherein the catalysts are firmly embedded in a silicon dioxide support film, so as to permit high resolution images of their surface structure at the onset of nanotube growth via the alcohol catalytic chemical vapor deposition process. We will report quantitiative measurements of catalyst coarsening, and discuss how this process plays a controlling role in nanotube nucleation and subequent growth. In each case, we will emphasize the power of the in-situ approach for providing quantiative data for discovering unique information regarding fundamental growth processes.

4:20pm **IE-MoA8 In-situ Probing and Manipulation of Dynamical Processes on the Nanoscale using Combined Scanning Tunneling and Transmission Electron Microscopy**, ***E. Olsson***, Chalmers University of Technology, Sweden **INVITED**

Properties on all scales are influenced and sometimes dominated by the atomic arrangement at individual defects and interfaces. Both scanning tunneling and transmission electron microscopy can be used to extract information about the structure of materials with high spatial resolution. The techniques are complementary where the scanning tunneling microscope (STM) allows us to image surfaces and perform spectroscopy on the nano- and subnanoscale. However, it is not possible to image and measure simultaneously. In addition, the images contain information about the surface while processes below the surface are not directly accessible. We have developed a combined STM and transmission electron microscopy (TEM) to enable the recording of dynamical processes on the nanoscale and direct correlation between local atomic structure and properties.[1] This talk will address experiments on carbon nanotubes including electromigration and a nanopipette function.[2] Another example concerns gold nanoparticles and the effect of laser irradiation on individual particles as well as ensembles of particles. An intense nanosecond laser pulse can cause melting, evaporation and diffusion which induce changes in particle size distribution, morphology, structural and properties.[3] Nanostructures are inherently small and often electron transparent without specimen preparation. However, it may be necessary to develop methods to extract the individual nanostructures or to manipulate and follow the changes of individual nanoparticles during dynamical processes. A combined focused ion beam workstation and scanning electron microscope with an in-situ manipulator provides the ability to reach into nanostructures and enables reproducible techniques of local extraction and identification.[3,4]

[1]K. Svensson, Y. Jompol, H. Olin and E. Olsson, Rev. Sci. Instr. 74, 4945 (2003).
[2]K. Svensson, H. Olin and E. Olsson, "Nanopipettes for Metal Transport", Phys. Rev. Lett. 93, 145901 (2004).
[3]L. Eurenius, K. Wettergren, Y. Alaverdyan, M. Käll, B. Kasemo, D. Chakarov and E. Olsson, "Microstructural changes in supported gold particle ensembles and individual particles upon pulsed laser irradiation", in manuscript.
[4]L. de Knoop, K. Svensson, H. Pettersson and E. Olsson, "Extraction of Individual Carbon Nanotubes for Local Probing of Transport Properties", AIP, 786, 118 (2005).

5:00pm **IE-MoA10 High-Resolution In-Situ Electron Microscopy Studies of Aqueous Samples**, ***N. de Jonge***, Oak Ridge National Laboratory, *D.B. Peckys,* University of Tennessee, Knoxville, *G.M. Veith,* Oak Ridge National Laboratory, *S. Mick,* Protochips Inc., *D.W. Piston,* Vanderbilt University, *S.J. Pennycook,* Oak Ridge National Laboratory, *D.C. Joy*, University of Tennessee, Knoxville

One of the main challenges of our time is the in-situ study of the molecular machinery of life in order to gain a fundamental understanding of how cells function at a molecular level. This challenge requires ways of imaging live cells. Recently, time-resolved confocal laser microscopy has been used to image protein function in living cells,[1] but this method's spatial resolution is on the order of the wavelength of light. Several new super-resolution techniques provide a high spatial resolution, but not temporal resolution.[2] We have begun applying electron microscopy (EM) to image cells in a liquid environment at atmospheric pressures. EM has sub-nanometer resolution and typically exhibits fast image acquisition. Others developed liquid enclosures for high-resolution imaging with transmission electron microscopy (TEM).[3] But, TEM imaging is sensitivite to materials with low atomic numbers, resulting in a strong background signal from the liquid and a low resolution for relevant volumes of liquid needed to image whole cells. Here, we present results from our new liquid scanning transmission electron microscopy (STEM) technique. STEM is insensitive to low z materials facilitating imaging through thicker samples. The liquid and the sample are enclosed between two ultra-thin windows of silicon nitride that are essentially electron transparent. Nanometer resolution and dynamic motion of gold nanoparticles enclosed in an aqueous environment will be reported. In addition we will present liquid STEM data from the high-resolution imaging of Ecoli bacteria labeled with quantum dots. Liquid STEM presents a new alternative to optical methods for time-resolved studies of intact Eukaryotic cells and bacteria. We are grateful to T. McKnight, R. Dona, G. Kremers, T.L. Harvey, C. Chisholm and P. Herrell. Research sponsored by the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory, managed by UT-Battelle, LLC for the U. S. Department of Energy under Contract No. DE-AC05-00OR22725.

[1] J. Lippincott-Schwartz, E. Snapp, A. Kenworthy, Nature Reviews 2, 444 (2001).

[2] V. Westphal, S. W. Hell, Phys. Rev. Lett. 94, 143903 (2005).

[3] M. J. Williamson, R. M. Tromp, P. M. Vereecken, R. Hull, F. M. Ross, Nature Materials 2, 532 (2003).

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