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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