

# 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 Ga<sub>2</sub>O<sub>3</sub> 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 (Fe<sub>2</sub>(CO)<sub>9</sub>) 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 H<sub>2</sub>O – 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 Al<sub>2</sub>O<sub>3</sub> 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 H<sub>2</sub> and H<sub>2</sub> + H<sub>2</sub>O 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 manufacturing, 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 micromechanics. 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  $\mu\text{m}$  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  $\text{TiO}_2$  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 incognita. 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  $\text{Cu}_2\text{O}$  islands during the transient oxidation of  $\text{Cu}(100)$ ,  $(110)$  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  $\text{Cu}_2\text{O}$  islands. For Cu-Ni oxidation, the addition of Ni causes the formation  $\text{Cu}_2\text{O}$  and/or  $\text{NiO}$  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).

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