Monday Afternoon, October 15, 2007

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 subsequent 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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