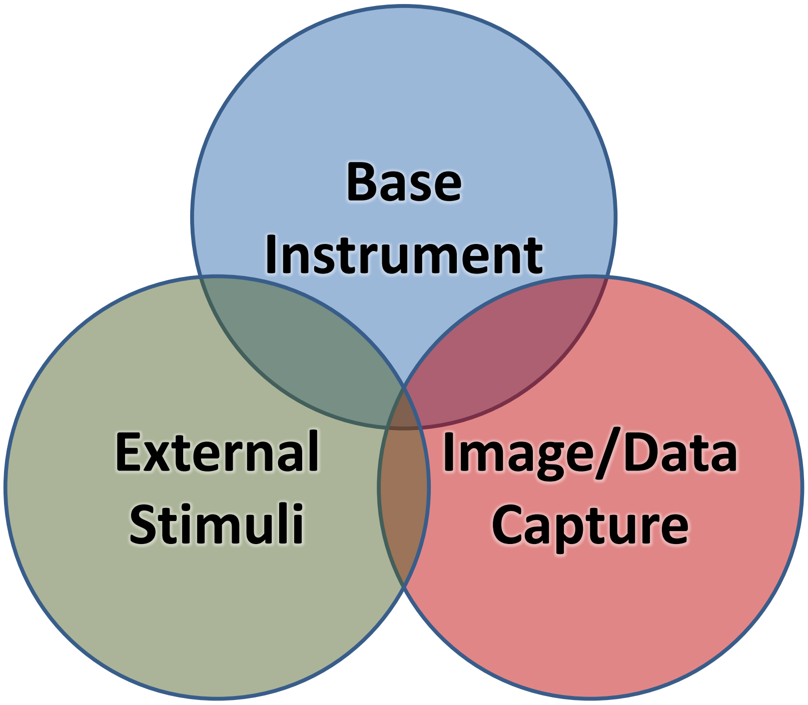
Frontiers of *In Situ* Transmission Electron Microscopy



Three aspects of *in situ* Transmission Electron Microscopy (TEM)

National Institute of Standards and Technology
Center for Nanoscale Science and Technology
Building 215, Rooms C103 - C106

Organizers:

Professor Mitra Taheri
Drexel University – Department of Materials Science and Engineering

Dr. Renu Sharma
National Institute of Standards and Technology – Center for Nanoscale Science and Technology

Dr. Eric Stach
Brookhaven National Laboratory – Center for Functional Nanomaterials

Program

April 11, 2013

7:30 - Registration + coffee

8:30 – Welcome (CNST Director Robert Celotta)

8:45 Introduction to meeting format (Mitra Taheri)

Session 1- External stimuli (Chair: Eric Stach)

9:00 Mechanical, electromechanical and optical *in situ* TEM probing techniques: **Andy Minor**, *Department of Materials Science & Engineering, University of California, Berkeley and National Center for Electron Microscopy, Lawrence Berkeley National Laboratory, One Cyclotron Road, MS 72, Berkeley, CA*

9:30 A brief history of quantitative TEM deformation technologies and some latest applications: **Zhiwei Shan**, *Center for Advancing Materials Performance from the Nanoscale (CAMP-Nano) & Hysitron Applied Research Centre in China (HARCC), State Key Laboratory for Mechanical Behaviour of Materials, Xi'an Jiaotong University, Xi'an, China*

10:00 Direct Imaging of Ferroelectric and Ferromagnetic Order and Switching in Nanostructured Materials Using *In-Situ* Electron Microscopy**:** S. D. Pollard, M.G. Han, V.V. Volkov and **Yimei Zhu,** *Condensed Matter Physics Department, Brookhaven National Laboratory, Upton, NY 11973; Department of Physics and Astronomy, Stony Brook University, Stony Brook, NY 11794*

10:30 Coffee Break and Poster Session

Session 2 External stimuli (continued)

11:00 Current and future perspectives on *in situ* electron microscopy using semiconductor-based active sample supports in heating and liquid environments, **Benjamin Jacobs**: *Protochips*

11:30 Transmission electron microscopy of nano-scale materials in liquid and gas environments: **Daan Hein Alsem,** *Hummingbird Scientific*

12:00 Boxed Lunch (Poster Session)

13:00 Give instructions for discussion groups (Renu Sharma-Eric Stach)

13:15 Discussion Session 1

15:00 Coffee Break and Poster Session

15:30 Presentation of findings of Discussion Session 1

Session 3 Introduction to ESTEM (Chair: Renu Sharma)

16:00 Image resolution and sensitivity in an aberration corrected environmental transmission electron microscope (ETEM) **Joerg R. Jinscheck**, *FEI Company, Materials Science BU, Achtseweg Noord 5, 5651 GG Eindhoven, The Netherlands*

16:30 Pursuing High Capability *In Situ* Gas ETEM – Instrumentation, Examples, and Challenges: **Xiao Feng Zhang**, Hitachi High Technologies America, Inc., 5960 Inglewood Drive, Pleasanton, CA 94588

17:00 Poster presentation and optional Facilities Tour (Alline Myers, Mihaela Tanase)

17:30 Adjourn

18:00 Shuttle Bus to Conference Dinner – Meet in Hilton Lobby

18:30 Conference Dinner – That's Amore Italian Restaurant
15201 Shady Grove Road, Rockville, MD 20850

April 12, 2013

Session 2- ETEM- (Chair: Renu Sharma)

8:30 Shining light on the Environmental TEM: **Jakob B. Wagner,** Filippo Cavalca, Thomas W. Hansen, *Center for Electron Nanoscopy, Technical University of Denmark, Kongens Lyngby, Denmark*

9:00 Environmental TEM for quantitative in-situ microscopy at the atomic scale: Seiji Takeda and Hideto Yoshida, *Institute of Scientific and Industrial Research (ISIR), Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan*

9:30 *Operando* TEM for Detection of Catalysis using Electron Energy Loss Spectroscopy: Benjamin K. Miller, Santhosh Chenna, and **Peter A. Crozier**, Arizona State University, Tempe, AZ 85281 (USA)

10:00 Coffee Break and Poster Session

10:30 Discussion Session 2

11:30 Presentation of findings from Discussion Session 2

12:00 Boxed Lunch

Session 3- Temporal resolution (Chair: Mitra Taheri)

13:00 Movie Mode Dynamic Transmission Electron Microscopy (DTEM): Multiple Frame Movies of Transient States in Materials with Nanosecond Time Resolution: **Thomas Lagrange,** Lawrence Livermore National Laboratory, Physical and Life Science Directorate, Condensed Matter and Materials Division, 7000 East Avenue, P.O. 808 L-356

13:30 K2-IS: A direct detection camera for high speed *in-situ* electron microscopy: **Ming Pan**, Gatan, Inc., 5794 W. Las Positas Blvd, Pleasanton, CA 94588

14:00 Discussion Session 3

15:00 Coffee Break and Poster Session

15:30 Discussion Session 3 (continued)

16:00 Presentation of findings of Discussion Session 3

16:30 Entire workshop discussion, including presentations by subgroups

17:30 Adjourn

Mechanical, electromechanical and optical *in situ* TEM probing techniques

Andrew M. Minor [1*]

[1] Department of Materials Science & Engineering, University of California, Berkeley and
National Center for Electron Microscopy, Lawrence Berkeley National Laboratory,
One Cyclotron Road, MS 72, Berkeley, CA USA
*Corresponding author's e-mail address: aminor@berkeley.edu

In situ transmission electron microscopy (TEM) provides dynamic observations of the physical behavior of materials in response to external stimuli such as temperature, environment, stress, and applied fields. In many cases, research is driven by the development of novel instrumentation and testing methodologies. One key advantage that probing techniques have is control over when the experiment begins. For example, is possible to keep a material undeformed until contacted by a mechanical probe such as an indenter. Or, it is possible to keep a material in a pristine state until probed by a lensed fiber optic for near-field optical probing. This talk will present recent developments from a number of in situ TEM probing techniques, including mechanical, electromechanical and optical probing. In the field of nanomechanics, *in situ* TEM holders have progressed to the level that we can measure both strength and ductility through quantitative compression, tension or bending experiments. These tests can also be extended to cryogenic (-140C) or elevated (400C) temperature. By augmenting the mechanical probing capabilities to include electrical measurements, it is possible to probe the coupled electrical and mechanical properties of materials such as piezoelectric thin films and functional nanomaterials. Lastly, recent results in optical near-field probing of laser-materials interactions will be discussed, including the development of an in situ Raman spectroscopy platform for a TEM.

A brief history of quantitative TEM deformation technologies and some latest applications

Zhiwei Shan[1]

[1]Center for Advancing Materials Performance from the Nanoscale (CAMP-Nano) & Hysitron Applied Research Centre in China (HARCC), State Key Laboratory for Mechanical Behaviour of Materials, Xi’an Jiaotong University, Xi’an, China, http://nano.xjtu.edu.cn

In this talk, following a brief review on the historical evolution of quantitative in situ deformation technologies, the applications of a recently developed in situ deformation technology will be reported. It was found that prior to the compression tests, the nickel pillars fabricated through Focused Ion Beam (FIB) were observed to contain a high density of defects. However, quite unexpectedly, the dislocation density was observed to decrease dramatically during the deformation process and, in some cases, even resulted in a dislocation-free crystal. The phenomena, which we termed as “mechanical annealing”, is the first direct observation of the dislocation starvation mechanism and sheds new light on the unusual mechanical properties associated with submicron- and nano- scale structures (Shan et al, Nature Materials, 2008). However, due to the dislocation core structure difference between the screw and edge dislocations in body centered cubic (BCC) metals, it was believed that BCC metals are incapable of mechanical annealing and the sample size strengthening behavior should be less that in FCC metals. By in situ compression of nanopillars inside a transmission electron microscope, we demonstrate that with the pillar diameter decreasing to hundreds of nanometers, significant mechanical annealing does occur in BCC Mo. In addition, there exists a critical size (DC ~ 200 nm for Mo at room-temperature) below which the strengthening exponent in Hall-Petch like regression increases dramatically to that similar to FCC metals. We attribute the observed phenomena to the diminishing importance of lattice friction at high stresses, when the size-enhanced flow stress exceeds a single screw dislocation’s lattice friction. At the end of this talk, the combination of this unique quantitative deformation technology with other hybrid stimuli, like electrical, thermal and even gaseous will be introduced.

Direct Imaging of Ferroelectric and Ferromagnetic Order and Switching in Nanostructured Materials Using In-situ Electron Microscopy

S. D. Pollard,[1,2] M.G. Han,[1] V.V. Volkov[1] and Y. Zhu[1,2]

[1] Condensed Matter Physics Department, Brookhaven National Laboratory, Upton, NY 11973
[2] Department of Physics and Astronomy, Stony Brook University, Stony Brook, NY 11794

We report our in-situ microscopy studies of ferromagnetic and ferroelectric order and switching to understand nanomagnetism, nanoferroelectricity, multiferroicity, and spin-electron correlations. Various case studies will be given: 1) Direct imaging precession obits of magnetic vortex-core with unprecedented spatial resolution to unravel the effects of spin transfer torque using GHz resonance current in patterned permalloy squares [1]; 2) The role of magnetic monopoles and Dirac string during magnetic reversal in frustrated artificial spin-ice lattices [2]; 3) Determining the ultimate scale limit of ferroelectric order and para- and ferro-electric transition in $BiTiO_3$ nanocubes [3]; and 4) Direct measurement of cation and anion displacement across ferroelectric domain walls in multiferroic $ErMnO_3$ single crystals [4]. The work was supported by U.S. Department of Energy, Office of Basic Energy Science, Material Sciences and Engineering Division, under Contract No. DE-AC02-98CH10886. Collaborations with members of the electron microscopy groups at BNL are acknowledged.

References

[1] SD Pollard, L Huang, KS Buchanan, DA Arena, Y Zhu, *Nature Communications*, **3**, 1028 (2012).
[2] SD Pollard, V Volkov, and Y Zhu, *Phys. Rev. B*, **85**, 180402(**R**), Editors' Suggestion, (2012).
[3] MJ Polking, MG Han, et al., *Nature Materials*, **11** 700-709 (2012).
[4] MG Han, Y Zhu, L. Wu, et al., *Advanced Materials*, in press.

Current and future perspectives on in situ electron microscopy using semiconductor-based active sample supports in heating and liquid environments

Benjamin Jacobs, Protochips, Inc., 616 Hutton St. Suite 103, Raleigh, NC 27606

The idea of in situ experiments in the electron microscope is nearly as old as the instrument itself. However, it took many decades before the tools and techniques were available to make in situ electron microscopy accessible to the EM community. Over the past several years, in situ microscopy has become more widespread to analyze materials in real-world conditions at the nano and atomic scale.

Creating tools for in situ TEM is challenging mainly due to the confined area in the column and small pole piece gaps frequently found in modern microscopes, which can be as small as 2 mm. To address this problem, many groups, including Protochips, are using fabrication techniques common in the semiconductor and MEMS industries to create devices with a high level of functionality in a small package. These techniques enable large-scale, reliable fabrication of windowed cells, which form the foundation of in situ liquid and gas systems now commercially available. Semiconductor devices are also an important component for the Protochips Aduro heating and electrical biasing system.

The semiconductor devices used as active sample supports for thermal experiments enable enhanced capabilities such as fast heating, stability and high level of temperature control. Results of atomic-resolution imaging and analysis at high temperatures will be presented. The thermal devices dramatically reduce thermal drift compared to other heating systems, and better control of the sample position as a function of temperature facilitates post-processed drift correction at higher magnification over larger temperature excursions. This keeps the area of interest in the field of view for easier analysis of materials during temperature changes. Results of recent work on drift correction will be discussed.

Liquid analysis in the TEM has generated much interest within several areas of research including nanomaterial synthesis and growth, biology and electrochemistry. It has been shown that a rotavirus sample can be imaged in water with a resolution as high as 25 Å, which is approaching resolutions typical in cryoEM for similar samples. This data along with a 3D reconstruction of rotavirus particles will be presented.

A caveat accompanying the new functionality provided by in situ techniques is the stream of new and possibly complicated data generated during experiments. This data is not always easily interpreted and in some scenarios may not be accurate, because miniaturizing the environment, especially in liquid and gas cell systems, can lead to misleading results. Other effects, such as the influence of the electron beam, must be taken into account as well. We are working to provide scientists with systems that provide more quantitative data, and these methods along with future perspectives will conclude the presentation.

Transmission electron microscopy of nano-scale materials in liquid and gas environments

Daan Hein Alsem – Hummingbird Scientific

Transmission electron microscopy (TEM) has an unmatched ability to characterize the structure and chemistry of materials at varying length scales via a combination of imaging, diffraction, and spectroscopy methods. To establish critical structure-property relationships *in operandi*, the use of TEM has moved beyond traditional post-mortem characterization, to a more relevant mode where many different *in situ* experiments are performed within the TEM. Conducting real-time observations of materials interactions at high spatial and temporal resolution in their native gas or liquid environment has attracted increasing attention across physical and biological science disciplines, with the promise of providing critical insight regarding the fundamental mechanisms that control the physiochemical properties of materials. A key challenge of this work has been the ability to contain a fluid (liquid or gas) in the high vacuum environment of the microscope, which has been accomplished via sealing the fluid inside a micro-fabricated cell with electron transparent membranes. In order to expand the versatility of this characterization approach, Hummingbird Scientific has developed two specialized *in situ* environmental fluid cell TEM specimen flow holders, one for experiments conducted in liquid and one for experiments in gas.

The liquid holder is being used to study nanoparticle growth, coalescence, and movement within a liquid layer. Additionally, *in situ* TEM studies have been used to monitor the structural evolution of deposited thin films samples held within the liquid cell, in order to study electrochemical processes. The liquid sample holder has also opened up new avenues in biological characterization of proteins and bacteria. The *in situ* atmospheric pressure gas specimen holder is being used to study gas catalysis reactions. The availability of these unique *in situ* holders has opened up new research directions that can be used to answer critical scientific questions regarding materials functionality for a broad range of materials. The recent results presented here summarize current capabilities for *in situ* microscopy using membrane-type environmental fluid cells, the use of which will allow researchers to perform a variety of *in operandi* studies of nano-scale energy and catalytic materials.

Image resolution and sensitivity in an aberration corrected environmental transmission electron microscope (ETEM)

Joerg R. Jinschek
FEI Company, Materials Science BU, Achtseweg Noord 5, 5651 GG Eindhoven, The Netherlands

Currently the strong focus on energy producing and environmental protecting technologies relies on the advancement of new functional nanomaterials, especially catalysts. Characterization of the state and properties of such a nanocatalyst as well as of the catalyst's activation, deactivation and poisoning demands detailed time resolved atomic-scale insights while in operation conditions [1,2]. In particular, visualization of solid heterogeneous catalysts and their structural evolution *in situ* under reaction environments are crucial to obtain detailed knowledge about the relationship between the nanostructure of the catalyst/support system and the actual reaction mechanism, because generally there is no evidence that the dynamic state of the materials can be truly inferred from postmortem examinations of the catalyst materials.

To our advantage, atomic-scale transmission electron microscopy (TEM), markedly advanced by utilizing hardware correctors compensating aberrations present in electromagnetic lenses [3], has become a powerful and indispensable tool for characterizing nanomaterials and provides this unique ability to image size, shape, as well as surface and interface structures of individual nanocatalysts [4,5]. The implementation of differential pumping apertures [6,7] in an aberration corrected environmental TEM (FEI Titan ETEM G2 [8]) enables to maintain these high-resolution imaging and analytical capabilities, while confining a gas environment in the close vicinity of the catalyst specimen [9].

Here we examine conditions to obtain such in situ observations in the high-resolution transmission electron microscopy (HRTEM) mode with an image resolution of 0.10 nm [10]. This HRTEM image resolution threshold is mapped out under different gas conditions, including gas types and pressures, and under different electron optical settings, including electron beam energies, doses and dose-rates. The 0.10 nm resolution is retainable for H_2 at 1-10 mbar. Even for N_2 the 0.10 nm resolution threshold is reached up to at least 10 mbar. The optimal imaging conditions are determined by the electron beam energy, dose-rate as well as the image signal-to-noise (S/N) ratio, that is consistent with Rose's criterion of $S/N \geq 5$. A discussion on the electron-gas interactions responsible for gas-induced resolution deterioration is given based on interplay with complementary electron diffraction (ED), electron energy loss spectroscopy (EELS) as well as scanning transmission electron microscopy (STEM) data [10].

Atomic-scale imaging in ETEM has opened up a unique possibility to monitor heterogeneous catalysts in their functional state [1,2]. This makes ETEM an essential complement to theoretical approaches as well as to the arsenal of established spectroscopic techniques that average information over length scales considerably larger than the characteristic dimensions of the nanostructures themselves.

[1] P. L. Hansen et al. Science 295, 2053 (2002).
[2] H. Yoshida et al. Science 335 (6066), 317 (2012).
[3] M. Haider et al. Nature 392, 768 (1998).
[4] C. Kisielowski et al. Angewandte Chemie Int. Ed. 49 (15), 2708 (2010).
[5] J.R. Jinschek, et al. Carbon 49, 556 (2012).
[6] E. D. Boyes, P. L. Gai. Ultramicroscopy 67, 219 (1997).
[7] R. Sharma, K. Weiss. Microscopy Research and Technique 42 (4), 270 (1998)
[8] http://www.FEI.com/ETEM
[9] T. W. Hansen et al. Mater. Sci. Technol. 26, 1338 (2010).
[10] J.R. Jinschek, S Helveg. Micron 43 (11), 1156 (2012).

Pursuing High Capability In Situ Gas ETEM – Instrumentation, Examples, and Challenges

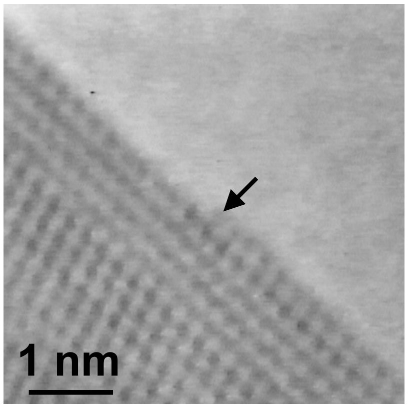
Xiao Feng Zhang

Hitachi High Technologies America, Inc., 5960 Inglewood Drive, Pleasanton, CA 94588.

Hitachi High Technologies Corporation, Tokyo 105-8717, Japan.

Conventional in situ transmission electron microscopy (TEM) performs work under a vacuum condition, it helps the real-time observation of changes in materials caused by external stimuli. However, because of the increasing involvement of solid-gas interaction in today's materials research such as studies on nanocatalysis, nanomaterial growth, and fuel cell materials, in situ TEM is required to be carried out with a gas supply to the specimen area. For this reason, the development of in situ environmental TEM (ETEM) technology has been moving fast in recent years.

Hitachi is actively pursuing the leading technologies in this field with a focus on high capability in situ heating gas ETEM. Hitachi's current emphases include high heating temperature (up to 1500°C), high flexibility for gas accommodation and gas pressure, high resolution real-time imaging (atomic level), and multiple in situ imaging modes. In this presentation, design of Hitachi ETEM, gas environmental-cell holder, and various in situ TEM specimen holders will be introduced accompanied with application examples in real scientific researches. Some immanent technical challenges for the in situ heating gas ETEM will be brought up for discussion.



SiC crystal growth at 1500°C. The real-time video shows a growing atomic layer on the top surface. Kamino et al, J. Electron Microsc. (Tokyo) **43** (1994) 104.

Shining light on the Environmental TEM

Jakob B. Wagner, Filippo Cavalca, Thomas W. Hansen
Center for Electron Nanoscopy, Technical University of Denmark, Kgs. Lyngby, Denmark

Digging into the world of photocatalysts by means of electron microscopy gives rise to new challenges. In order to study photocatalysts under working conditions, a holder capable of exposing a sample to visible light *in situ* during gas exposure in the ETEM has been developed at DTU Cen[1]. One of the major challenges when studying the effects of visible light in the electron microscope is to differentiate between the effect of visible light and that of high-energy electrons. New protocols for acquisition and robust interpretation of *in situ* data on photocatalysts are needed to minimize the effect of the electron beam without compromising image quality and information to exploit the full potential of *in situ* light stimuli.

A major parameter degrading the image quality in ETEM is the gas-electron interactions. Even though high-resolution ETEMs have been around for more than a decade little has been done in trying to understand the effects of gas-electron interaction on the image formation[2-4].

The addition of aberration correction and monochromation to ETEM has improved the point resolution and reduced image delocalization allowing for a more direct interpretation of surfaces and interfaces. Recently Yoshida *et al.* reported transmission electron microscopy imaging of CO molecules adsorbed on Au nanoparticles[5]. However, when gas is present in the microscope column the electron wave is modified due to gas-electron interactions[6, 7]. Several factors have to be taken into account when combining high-energy electrons with a gaseous environment. The fast electrons are scattered both elastically and inelastically by the gas molecules resulting in distortions of the electron wave both above and below the sample, thus altering the incoming and the exit wave carrying the image information. Furthermore, the interaction between fast electrons and gas molecules leads to ionization of the gas molecules. A full understanding of both the interaction of fast electrons with gas molecules and the effect of gas on high-resolution imaging is therefore necessary to take the next step towards quantitative ETEM.

Here, the case study of *in situ* Cu_2O photocorrosion is presented together with our ongoing work involving systematic measured images, diffraction patterns and energy-loss spectra acquired in gases in order to elucidate the influence of gas-electron interaction under imaging conditions suitable for *in situ* light experiments.

[1] F. Cavalca, A. B. Laursen, B. E. Kardynal, R. E. Dunin-Borkowski, S. Dahl, J. B. Wagner, and T. W. Hansen, Nanotechnology **23** (2012).
[2] H. Yoshida and S. Takeda, Phys. Rev. B **72**, 195428 (2005).
[3] A. N. Bright, K. Yoshida, and N. Tanaka, Ultramicroscopy **124**, 46 (2013).
[4] T. W. Hansen and J. B. Wagner, Microscopy and microanalysis : the official journal of Microscopy Society of America, Microbeam Analysis Society, Microscopical Society of Canada **18**, 684 (2012).
[5] H. Yoshida, Y. Kuwauchi, J. R. Jinschek, K. Sun, S. Tanaka, M. Kohyama, S. Shimada, M. Haruta, and S. Takeda, Science **335**, 317 (2012).
[6] T. W. Hansen, J. B. Wagner, and R. E. Dunin-Borkowski, Materials Science and Technology **26**, 1338 (2010).
[7] T. Yaguchi, M. Suzuki, A. Watabe, Y. Nagakubo, K. Ueda, and T. Kamino, Journal of Electron Microscopy **60**, 217 (2011).

Environmental TEM for quantitative in-situ microscopy at the atomic scale

Seiji Takeda and Hideto Yoshida
Institute of Scientific and Industrial Research (ISIR), Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan

We summarize our recent in-situ ETEM studies on metal nanoparticle catalysts to describe the issues surrounding the application of ETEM to catalyst chemistry[1] for this workshop. The recently developed ETEMs can work robustly, so we can accumulate observation data in controlled environments.

First we deal with the electron irradiation effect. We established a structural evolution diagram that summarizes the structure of catalysts under electron irradiation as a function of the electron current density φ, and the electron dose, D. By extrapolating to $\varphi=0$, $D=0$, we could deduce the catalysis structure without electron irradiation in reaction environments. In gold nanoparticulate catalysts that work for the oxidation of CO at room temperature, for instance, the surfaces of the nanoparticles are thought to be covered with CO molecules in reaction environments. To confirm that CO gas molecules are adsorbed on the surfaces in a steady state even under electron irradiation, we estimated the rates of adsorption and desorption of CO on the surfaces. For a typical reaction environment in ETEM, we estimated the rates of thermal desorption, electron-stimulated desorption and knock-on desorption. The rate of adsorption was also estimated from the sticking rate. CO was consumed because of its oxidation by the catalyst and the oxidation rate of CO per surface gold atom was estimated using catalytic chemical measurements. As a result, the adsorption rate was larger than the sum of the desorption rates and the oxidation rate. This analysis concluded that CO dominated the surfaces of the nanoparticles in the reaction environment, even under electron irradiation.

Second we deal with the heterogeneity of real catalysts. The microstructures of chemically synthesized catalysts are structurally heterogeneous. Nanoparticles in real catalysts have different atomic structures, although their size is well controlled. The question is whether a nanoparticle under ETEM observation at higher magnification is responsible for the catalytic activity or not. Since there is no microscopic method that can directly estimate the catalytic activity of a nanoparticle in a real catalyst, we must perform the statistical and numerical analysis of substantial amounts of ETEM data to determine the behavior of nanoparticles that is correlated with the catalytic activity. We established a morphology phase diagram of gold nanoparticulate catalysts that summarizes how the majority of nanoparticles change their morphology systematically as a function of the partial pressures of gases. This also suggested that O_2 molecules are preferentially dissociated at the perimeter interface between gold nanoparticles and a support. Similar diagrams will be helpful in elucidating the phenomena that directly correlate with the catalytic activity determined from ETEM observations.

As a summary, high-spatial and time resolutions are necessary preconditions for the application of ETEM to catalyst chemistry, but they are not sufficient to ensure success. An ETEM that works robustly to accumulate observation data is essential. Hence, the field of quantitative in-situ ETEM is only in its beginning stages.

This research was supported by Grant-in-Aid for Specially Promoted Research Grant No. 19001005 from the Ministry of Education, Culture, Sports, Science and Technology (MEXT).

Reference:

1. S. Takeda and H. Yoshida, Microscopy 62 193-203 (2013).

Operando TEM for Detection of Catalysis using Electron Energy Loss Spectroscopy

Benjamin K. Miller, Santhosh Chenna, and Peter A. Crozier*
[1]Arizona State University, Tempe, AZ 85281 (USA)
*crozier@asu.edu

Understanding structure-reactivity relations for catalysts is essential in developing a fundamental understanding of the functionality of catalytic materials. The structure of a catalyst depends on several factors, such as temperature, pressure, reactant gases, product gases, and concentration of different gas species on the surface of the catalyst. Thus, in order to obtain information on the active state of a catalyst, it is important to apply *in-situ* techniques that allow catalyst structure to be determined while catalytic reactions are taking place i.e. under the working conditions. *In-situ* environmental transmission electron microscopy (ETEM) is a powerful tool to study dynamic gas-solid interactions under reacting gas conditions at elevated temperatures and is ideal for studying high surface area materials that are often used as catalysts. The ability to study catalytic materials at elevated temperatures in the presence of reactive gases can provide fundamental insights into the catalyst synthesis and its dynamic evolution during a catalytic reaction. It would be highly desirable to measure the activity and selectivity of the catalyst simultaneously with the structure so that the structure and reactivity could be directly correlated. This approach gives rise to the so-called *operando* methods first pioneered for Raman spectroscopy.

Until recently, true *operando* microscopy characterization was demonstrated for applications such as catalytic growth of polymers, nanotubes and nanowires where the catalytic products were solids which can be directly imaged. For gas phase reactions, the reactant and product gases are not directly visible with microscopy imaging and diffraction techniques and so suitable spectroscopic methods must be developed to detect the product gas molecules. We demonstrated that electron energy loss spectroscopy (EELS) in the TEM can be used to quantify the gas composition inside the reaction cell.[1] Recently we extended this approach to demonstrate that catalytic products can be detected and quantified inside the microscope reaction cell while simultaneously determining the nanoscale structure of the catalyst[2]. One advantage of using EELS is that the composition of the volume of gas adjacent to the TEM sample is directly measured. EELS is available on many microscopes and this approach can be applied to ETEM based on differentially pumped cells, windowed cells or cells fitted with injection needles.

References

1. Crozier, P. A. and S. Chenna (2011). "In situ analysis of gas composition by electron energy-loss spectroscopy for environmental transmission electron microscopy." Ultramicroscopy **111**(3): 177-185.

2. Chenna, S. and P. A. Crozier (2012). "Operando TEM: A technique for detection of catalysis using electron energy-loss spectroscopy in transmission electron microscope." ACS Catalysis **2**: 2395-2402.

3. This project is supported by National Science Foundation CBET-1134464.

Movie Mode Dynamic Transmission Electron Microscopy (DTEM): Multiple Frame Movies of Transient States in Materials with Nanosecond Time Resolution

Thomas LaGrange

Lawrence Livermore National Laboratory, Physical and Life Science Directorate, Condensed Matter and Materials Division, 7000 East Avenue, P.O. 808 L-356

Most processes in materials naturally occur in conditions far from equilibrium on short time scales, ranging from the femtosecond-scale processes occurring from non-equilibrated electron states to microsecond transient events of phase transformations and deformation processes. Typically, we are confined in the laboratory to conduct experiments near equilibrium or observe material post process due to the resolution limitations of conventional analytical techniques. Though insight about material's behavior gained from these observations, much of coupled and convoluted events of complex processes not well understood that limit and require technique that both high spatial and temporal resolution to observe nanoscale microstructural features evolving on short timescales. In effort to meet the need for studying fast dynamics and transient states in material processes, we have constructed a nanosecond dynamic transmission electron microscope (DTEM) at Lawrence Livermore National Laboratory to improve the temporal resolution of in-situ TEM observations.

Prior DTEM hardware only allowed single-pump/single-probe operation, building up a process's typical time history by repeating an experiment with varying time delays at different sample locations. Movie Mode DTEM upgrade now enables single-pump/multi-probe operation. These technical improvement provide the ability to track the creation, motion, and interaction of individual defects, phase fronts, and chemical reaction fronts, providing invaluable information of the chemical, microstructural and atomic level features that influence the dynamics and kinetics of rapid material processes. For example, the potency of a nucleation site is governed by many factors related to defects, local chemistry, etc. While a single pump-probe snapshot provides statistical data about these factors, a multi-frame movie of a unique event allows all of the factors to be identified and the progress of nucleation and growth processes can be explored in detail. It provides unprecedented insight into the physics of rapid material processes from their early stages (e.g. nucleation) to completion, giving direct, unambiguous information regarding the dynamics of complex processes. This presentation will discuss the technical aspects of the Movie Mode DTEM technology in the context of recent material science studies using the novel *in situ* TEM capability.

Work preformed at LLNL under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344 and supported in part by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering.

K2-IS: A direct detection camera for high speed *in-situ* electron microscopy

Ming Pan and Cory Czarnik
Gatan, Inc., 5794 W. Las Positas Blvd, Pleasanton, CA 94588

In-situ electron microscopy is undergoing another rapid phase of growth and has become an indispensable tool in materials design, testing and discovery. The dynamic observation for a range of scales down to the atomic level allows users to gain valuable insight on structure-function-performance relationship of materials across a wide range of applications.

In-situ electron microscopy is heavily dependent on hardware instrumentation development (microscopes, specimen holders, and imaging detectors.) While advancements have been made in new microscope technology (environmental TEMs and aberration corrections) and various *in-situ* TEM holders (MEMS heating, liquid and gas cell, nano/pico-indentation devices, etc.) progress in developing imaging detectors optimized for *in-situ* applications has been slow until a combination of technologies have recently come together to enable high sensor performance along with super-fast data rate processing, transfer, and storage.

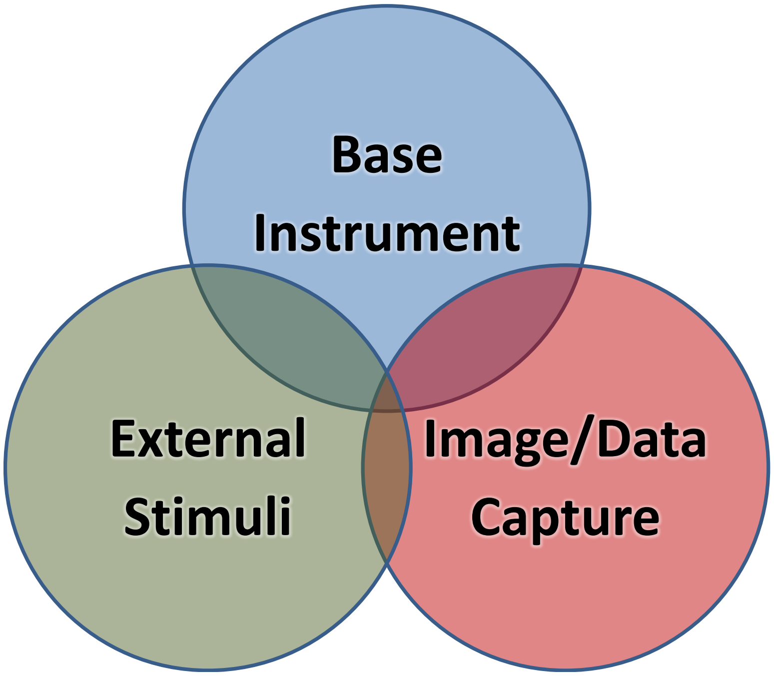
Direct detection cameras form electron images by directly detecting high energy electrons incident on an active pixel CMOS (complementary metal-oxide-semiconductor) sensor. The elimination of a scintillator and optical transfer path (lens or fiber-coupling) has significantly improved the detection quantum efficiency (DQE) of the camera, increasing the signal-to-noise ratio of each electron that reaches the sensor.

Today there is a chasm between traditional *in-situ* experiments (tens of frames per second) and DTEM (dynamic TEM) experiments (temporal resolution of pico- or femto- second). It is highly desirable to have the temporal resolution in the microsecond or beyond. Combined with high speed data communication and processing technologies Gatan K2-IS (*in-situ*) direct detection camera has been developed to capture usable sub-frames at up to 1600 frames per second. Continuous images generated at this speed can be processed and streamed to storage in real-time, thus generating enormous amount of data; this requires new algorithm and computer programs to be developed for viewing and analysis.

With the development of Gatan K2-IS direct detection camera *in-situ* microscopy is entering an unexplored territory full of opportunities. In this presentation the design of K2-IS will be presented along with preliminary results obtained.

Frontiers of
In Situ Transmission Electron Microscopy

Poster Abstracts



Visualizing Dynamic Processes in TEM Using a Direct Detection Device

Liang Jin, Benjamin E Bammes, Dong-Hua Chen and Robert B. Bilhorn

Direct Electron, LP, San Diego, CA, USA

Transmission electron microscopy (TEM) is a powerful technique for visualizing dynamic processes at nanometer or Angstrom resolution. Increasingly, existing TEM camera performance is not able to keep up with the demanding requirements of in-situ experiments, where large field of view, high signal-to-noise ratio (SNR) and high temporal resolution are all important factors.

As a pioneer in the development of high performance direct electron detectors for TEM, Direct Electron, LP (San Diego, CA, USA) introduced the first large-format Direct Detection Device (DDD®) in 2008, as the culmination of academic and industrial partnerships working through six generations of sensor development beginning in 2001. Recently, Direct Electron released a new generation of software to enable the award-winning DE-12 DDD camera to be used in in-situ TEM, with unlimited continuous streaming capability at 12-megapixels resolution at 40 fps and a higher MTF than any CCD cameras on the market. The unique high speed readout of the DDD technology allows parallel readout during the exposure and thus creating a continuous movie with virtually 100% duty cycle, a dramatic improvement over CCD camera whose readout time becomes a significant burden on duty cycle when operated at high frame rate.

We will present the principles and design of the DDD cameras and the latest experimental results from academic collaborators utilizing the movie readout feature.

Title: Unusually sharp paramagnetic phase transition in thin film Fe_3Pt invar
Authors: Jasper Drisko and John Cumings, University of Maryland

Invar alloys, typically 3d transition metal rich systems, are most commonly known for their extremely low coefficients of thermal expansion (CTE) over a wide range of temperatures close to room temperature. This anomalous behavior in the CTE lends Invar to a variety of important applications in precision mechanical devices, scientific instruments, and sensors, among others. Many theoretical models of Invar have been proposed over the years, the most promising of which is a system described by two coexisting phases, one high-spin high-volume and the other low-spin low-volume, that compete to stabilize the volume of the material as the temperature is changed. However, no theory has yet been able to explain all experimental observations across the range of Invar alloys, especially at finite temperature [1]. We have fabricated thin films of a Fe_3Pt Invar alloy and investigate them using Lorentz Transmission Electron Microscopy (TEM). 23nm films are deposited onto SiN membrane substrates via radio-frequency magnetron sputtering from a pure Fe target decorated with Pt pieces. The film composition is characterized using wavelength dispersive spectroscopy (WDS) in a JEOL JXA-8900 Superprobe. We observe novel magnetic domain structures and an unusually sharp phase transition between ferromagnetic (FM) and paramagnetic (PM) regions of the film under a temperature gradient. This sharp transition suggests that the FM-to-PM transition may be first order, perhaps containing a structural-elastic component to the order parameter. However, electron diffraction reveals that both the FM and PM regions have the same FCC crystal structure.

[1] Kakehashi, Y., *Phys. Rev. B.* **38**, 474 (1988).

KHIM KARKI-UNIVERSITY OF MARYLAND

Real-time investigation of engineered silicon nanostructures for lithium-ion battery electrodes

Khim Karki[1], Chuanfu Sun[2], Eric Epstein[1], Jeong-Hyun Cho[3], Zheng Jia[4], Teng Li[4], Yue Qi[5], Tom Picraux[3], Chunsheng Wang[6], YuHuang Wang[2], and John Cumings[1]

1 Materials Science & Engineering, University of Maryland, College Park, Maryland
2 Department of Chemistry & Biochemistry, University of Maryland, College Park, Maryland
3 Los Alamos National Laboratory, Los Alamos, New Mexico
4 Department of Mechanical Engineering, University of Maryland, College Park, Maryland
5 General Motors Research, Warren, Michigan
6 Chemical & Biomolecular Engineering, University of Maryland, College Park, Maryland

Silicon-based anode materials are an attractive candidate to replace today's widely-utilized graphitic electrodes for lithium-ion batteries because of their high gravimetric energy density (3572 mAh/g vs. 372 mAh/g for carbon) and relatively low working potential (~ 0.5V vs. Li/Li$^+$). However, their commercial realization is still far away because of the structural instabilities associated with huge volume changes of ~300% during charge-discharge cycles. While cracking and pulverization are known to be mitigated in part by nanostructured forms of silicon, such as nanowires, several recent studies indicate that cracking can still occur in nanostructures under a variety of conditions. With real-time studies using a specialized transmission electron microscopy (TEM) platform, we observe an opposite effect in which physically distinct silicon nanowires (SiNWs) can become fused through an electrochemically-induced process, which suggests that this welding may lead to self-healing in nanostructured Si-electrodes. Our results show evidence of robust weld strength and facile transport of lithium ions across the welded Si-Si interface, both desirable properties for enhanced battery performance. Similarly, CNT@α-Si beaded-string heterostructures with chemically tailored carbon–silicon interfaces were designed and synthesized based on a fundamental understanding of carbon surface chemistry and Si nucleation on covalently modified CNT surfaces. *In situ* TEM studies of lithiation propagation reveal that these novel heterostructures can accommodate massive volume changes during lithiation and delithiation without appreciable mechanical failure. These findings thus provide important new insights in the design of high performance Si electrodes, laying a foundation for next-generation lithium ion batteries.

This work is supported by the US Department of Energy, Office of Basic Energy Sciences as part of an Energy Frontier Research Center.

References
[1] Ryu et al., *J. Mech. Phys. Solids.* 59, 1717-1730 (2011).
[2] Li et al., *J. Electrochem. Soc.* 158 (6), A689-A694 (2011).
[3] Goldman et al., *Adv. Funt. Mater.* 21, 2412-2422 (2011).
[4] Liu et al., *Nano Lett.* 11, 3312-3318 (2011).

This work is supported by the US Department of Energy, Office of Basic Energy Sciences as part of an Energy Frontier Research Center.

The Liquid Cell – An In Situ Measurement Platform for Energy Materials and Devices

M. Tanase[1,2], R. Sharma[1], V. Aksyuk[1], G. Holland[1], A.Liddle[1]

[1]Center For Nanoscale Science and Technology, National Institute of Standards and Technology, 100 Bureau Drive, Gaithersburg, MD 20899; [2] Institute for Research in Electronics and Applied Physics, University of Maryland, College Park, MD 20742

Except in a very few special cases, liquids are incompatible with the vacuum environment of the transmission electron microscope. However, many scientifically interesting and industrially important processes take place in liquids: electrochemistry and catalysis are two that are vital in many applications, not least energy generation and storage. Understanding the processes that, for example, lead to loss of storage capacity in batteries, or loss of reactivity due to catalyst agglomeration, sintering or poisoning is critical. There is thus a growing need for developing metrologies where the system components can be studied in their reactive environments. Although we can perform in situ nanoscale measurements of catalytic processes in gaseous environments using an environmental scanning/transmission electron microscope (ESTEM), comparable measurements in liquids are much more challenging.

We present a new MEMS-based measurement platform for studying systems in liquid/gaseous environments inside the Transmission Electron Microscope (TEM). The platform takes advantage of the high spatial resolution of the TEM, and allows the application and measurement of electrical signals and the possibility of working in controlled gaseous or liquid environments, *in situ* in the TEM. The platform consists of disposable liquid and environmental cells mounted on a specimen insertion holder with the ability to control a microfluidic flow and the ability to apply and measure electrical signals in the pA range. The cell has an electron-transparent investigation area consisting of liquid confined between silicon nitride membranes, an electron-transparent electrode, reference and current collectors. The cell also contains an interfacing system to an external microfluidic circuit controlled by a syringe pump, and to a sub-nA electrical signal processing system, both supported by the specimen insertion holder, which also provides an air-vacuum interface and an X-ray screening shield compatible with conventional, high-vacuum transmission electron microscopes. Our design addresses issues raised by already-existing encapsulation solutions for TEM in that it provides a fine control of the liquid thickness across the entire electron-transparent area, thus making imaging and quantization using analytical techniques such as EELS and EFTEM possible; it provides simultaneous microfluidic flow control and application/measurement of electrical signals; and it is much less prone to contamination, a major issue in TEM. The platform is self-contained and maintains compatibility with other investigation techniques such as STEM, FESEM, FIB and XRD. It will allow a suite of metrologies already available in the TEM to be coupled with electrical measurements in controlled environments, in order to characterize dynamic processes relevant to energy materials and devices, in situ and with nanoscale spatial resolution.

Quantification of In-Situ S/D/TEM Observations in the Liquid Stage

I. Arslan[1], J. E. Evans[2], L. R. Parent[3], P. Abellan[1], T. J. Woehl[3], M. Gu[2], L. Mehdi[1], W. D. Ristenpart[3], C. Wang[2], and N. D. Browning[1]

[1] Fundamental and Computational Sciences Directorate, Pacific Northwest National, Laboratory, P.O. Box 999, Richland, WA 99352 USA

[2] Environmental Molecular Sciences laboratory, Pacific Northwest National, Laboratory, P.O. Box 999, Richland, WA 99352 USA

[3]Department of Chemical Engineering and Materials Science, University of California-Davis, One Shields Avenue, Davis, CA 95616. USA

Many processes in materials chemistry are dependent on the local environmental conditions (temperature, voltage, stress, gas, liquid etc). Therefore, although recent years have seen a paradigm change in (scanning) transmission electron microscopy with unprecedented improvements in spatial, spectroscopic and temporal resolution being achieved, a full utilization of these new capabilities *to study processes* requires precise control of the environment around the sample. Here we present the development and implementation of the in-situ liquid stage that permit the study of samples in solution. Obtaining reproducible and quantifiable results requires a complete calibration of the effect of the electron beam on the process being studied. After calibration, detailed quantitative measurements of the nucleation and growth of individual nanoparticles or different phases within nanoparticles can be determined and compared directly with ex-situ results. As these stages can be incorporated into both high spatial resolution aberration corrected (S)TEM, as well as into the high temporal resolution Dynamic TEM (DTEM), the specifics of the measurements for both types of microscopes will be described, and results from all of the liquid stage research performed at PNNL will be represented.

Pacific Northwest National Laboratory is operated by Battelle Memorial Institute for the U.S. Department of Energy under Contract No. DE-AC05-76RL01830. Development of in-situ stages was supported by DOE NNSA-SSAA grant number DE-FG52-06NA26213, NIH grant number RR025032-01, and the Presidential Early Career Award for Scientists and Engineers.

Development of Biasing Holders in the Dynamic Characterization Group

H. Ghassemi, A. Lang, W. Harlow, M.L. Taheri

Department of Materials Science and Engineering, Drexel University, Philadelphia, PA 19104

Abstract

This work presents recent progress and developments made in *in-situ* transmission electron microscopy by the Dynamic Characterization Group (DCG) at Drexel University. We present results obtained with conventional biasing and a developed environmental holder.

We investigated the failure mechanism of AlGaN/GaN high-electron mobility transistors (HEMTs) during real-time performance. AlGaN/GaN HEMTs have applications as high-power and high-frequency devices; however, high-power operating conditions can result in unpredictable and catastrophic device degradation. Although the majority of current researchers study these devices using cathodoluminescence (CL), AFM or even simulation, little is known about their reliability and degradation mechanism. We successfully biased individual devices inside the TEM using a conventional biasing holder in order to observe and characterize the onset of formation of defects and their structural evolution. Our ultimate goals are to identify the specific onset of formation of defects, simultaneously measure the electrical bias signals of the device, and correlate the structural evolution to the breakdown in the device electrical properties.

Biasing experiments can be developed in conjunction with other external stimuli such as gas and liquid environments. We present results of an environmental holder which utilizes a MEMS device as a heating/biasing platform in order to study electrochemical processes and corrosion. TiO_2 has several applications in fields such as photocatalysis, lithium-ion batteries, and biotechnology. It forms three main polymorphs which include rutile, anatase, and brookite. Rutile is the most stable form of TiO_2 while the others are considered metastable. Anatase stabilizes by converting to rutile at a wide range of temperatures, which can be affected by oxygen defect level or presence of dopants. Therefore, understanding the nature of this transformation as well as the effect of atmosphere on the kinetics is important to further develop TiO_2 applications. Experiments were carried out under various gas flows of up to 1 atm. The as-grown nanoparticles were anatase TiO_2. Both "bare" particles and particles coated with a nanoscale carbon shell were studied. HR-TEM images and diffraction patterns confirmed the anatase structure of the initial product. Atmospheres in this study included vacuum, nitrogen, oxygen and argon pure gases. The temperature was increased to 1000°C, under different gas exposures, until the phase transition from anatase to rutile was detected.

Authors acknowledge Professor H. Xing and her group at University of Notre Dame, Professor Rasit Koc at Southern Illinois University, Protochips for holder development, and support from the Office of Naval Research through code 312 "Electronics, Sensors, and Network Research," under contract number ONR- N00014-11-1-0296.

In-Situ Transmission Electron Microscopy of Charge Ordered Materials Gated by Ionic Liquid

J.D. Sloppy[1], A.C. Lang[1], R.Devlin[1], H. Ghassemi[1], R. Sichel-Tissot[1], S.J. May[1], J.C. Idrobo[2], M.L. Taheri[1]

1. Materials Science and Engineering Department, Drexel University, 3141 Chestnut Street, Philadelphia, PA 19104-2816, U.S.A.
2. Materials Science & Technology Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831-6069, U.S.A.

Electronic devices such as field effect transistors use an applied bias to induce a metal-insulator transition. Charge ordered materials are studied as possible future materials for transistor applications. One such material is $La_{1/3}Sr_{2/3}FeO_3$ (LSFO), which has an insulator-metal transition at 190 K. Below the transition temperature, the charge on Fe atoms is ordered in the <111> direction as …$Fe^{3+,}$ Fe^{3+}, Fe^{5+}... above the transition temperature, the Fe valence is disordered with an average value of 3.7, and the material is an insulator.

The charge-ordering transition has been observed in bulk ceramics using electron diffraction in the TEM,[1] and synchrotron X-ray diffraction has demonstrated charge ordering in our relatively thick films grown by MBE. However, as the need to characterize thinner layers of charge ordered material increases, the spatial resolution and relative convenience of cryo-TEM is necessary for the measurement of charge ordering. The effects of biasing on the electrical properties and on charge-ordering can also be studied using *in-situ* TEM. In an effort to simultaneously measure the effects of biasing and temperature, we explore the use of an ionic liquid to freeze in charge accumulation in lieu of maintaining an applied bias during TEM measurements.

Ionic liquids are gaining popularity as a way of achieving charge accumulation at an interface without maintaining an external, applied bias. Sheet carrier densities on the order of $10^{14}/cm^2$ have been reported[2], which is greater than can be typically obtained by applying a bias. We are exploring the use of ionic liquids as a method of measuring electronic characteristics analogous to what could be measured using *in-situ* biasing measurements. Specimens are prepared using the focused ion beam (FIB) and preliminary STEM-EELS have demonstrated the feasibility of studying changes in the electronic structure as a function of accumulated charge density.

The use of ionic liquids as a means of forcing charge accumulation can be combined with *in-situ* TEM techniques such that the effects of bias and another variable (such as strain, temperature, or atmosphere) can be examined simultaneously with existing TEM holders.

[1] S.K. Park, *et.al.*, *Phys. Rev. B*,. 60 (1999) 788.
[2] S. Asanuma *et.al. App. Phys. Lett.* 97 (2010) 142110.

This research was supported by the Office of Naval Research under grant N00014-11-1-0664. This research was supported in part by Oak Ridge National Laboratory's Shared Research Equipment (ShaRE) User Program (JCI), which is sponsored by the Office of Basic Energy Sciences, U.S. Department of Energy.

EMSL *In Situ* TEM Capabilities

B. Kabius, L. Kovarik, C. Wang;

Pacific Northwest National Laboratory

Recently installed new equipment has expanded the microscopy capabilities at EMSL greatly, allowing micro-structural research under *in situ* conditions. Several state-of-the art instruments, including an image corrected environmental TEM (ETEM) and a probe corrected STEM, are already in place and more are to follow. These microscopes are housed in a new building which provides an optimum environment for equipment sensitive to vibrations and magnetic field.

Attached to these instruments are customized probes that lend, ultimately enhance, the instruments the capabilities for designing of experiments under in-situ/operando conditions. The abilities of these instruments and how they have been applied to catalysis and energy storage research will be discussed. Future project which are focused on improving time resolution for observing dynamic processes will be outlined.

Sponsored by:

Center for Nanoscale Science & Technology
National Institute of Standards and Technology
100 Bureau Drive, MS 6200
Gaithersburg, MD 20899-6200

JEOL USA, Inc.
11 Dearborn Road
Peabody, MA 01960

FEI Company
5350 NE Dawson Creek Drive
Hillsboro, Oregon 97124 USA