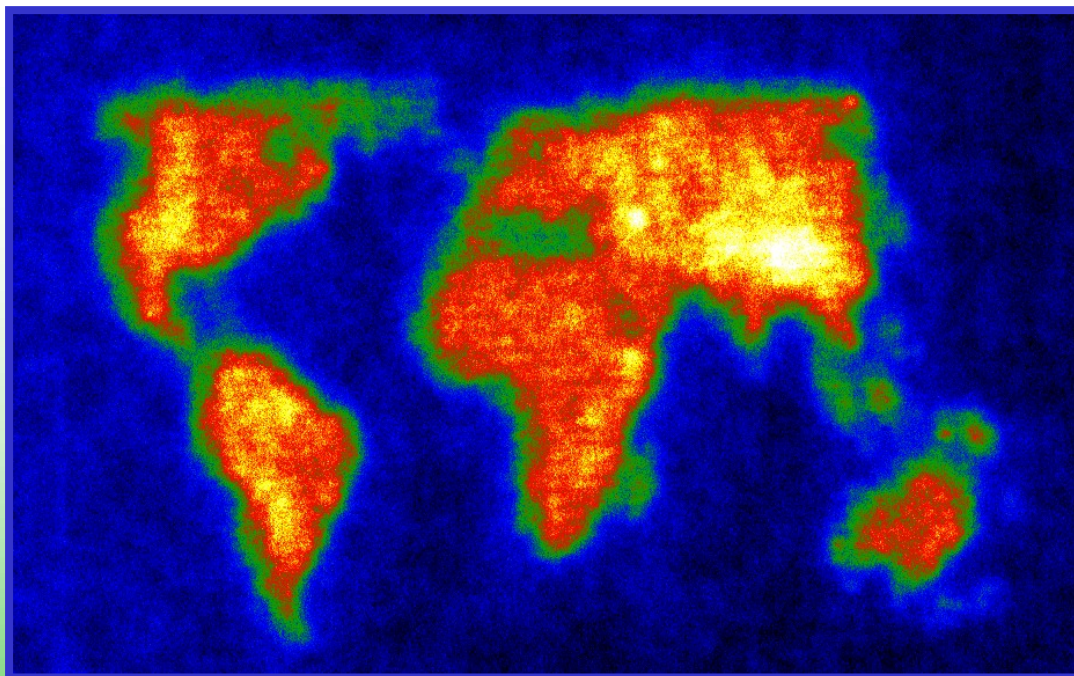**NSF Workshop Report on**

Dynamic *in situ* electron microscopy as a tool to meet the challenges of the nanoworld

**The Buttes
Tempe, Arizona**

January 3 – 6, 2006

230 nm

Dynamic *in situ* electron microscopy as a tool to meet the challenges of the nanoworld

Report of a workshop held at
The Buttes Resort, Tempe, Arizona
January 3–6, 2006

R. Sharma (Chair)
P. A. Crozier and M. M. J. Treacy

Front page picture is nanoscale map of the world drawn using electron beam induced deposition (EBID) with W based precursor on silicon nitride substrate (Courtesy P.A. Crozier (ASU) and W. van Dorp (TU, Delft)). Nano Saguaro (courtesy of M.M.J. Treacy (ASU)).

Dynamic *in situ* electron microscopy as a tool to meet the challenges of the nanoworld

Summary

Workshop Overview and Objectives

We are now in an era where the scale of materials structures required for technology is shrinking at a fast pace. Transmission electron microscopy (TEM) and related techniques are primary characterization tools for this nanoworld. Recent developments in instrument design and auxiliary equipment have made it possible to synthesize, characterize and measure properties of active materials at the nanoscale, *in situ*, using TEM. Various *in situ* and *operandi*[†] techniques have emerged in recent years and are assuming greater importance in different areas of science and engineering. In this report, we use the term '*in situ* TEM' to apply to experiments where some form of stimulus is applied to a sample while it is observed in a TEM. The main objective of this workshop was to identify current and future research programs where *in situ* observation of dynamic processes can lead to greater understanding and control of nanomaterials synthesis and properties.

This workshop was held at the *Buttes Resort* in Tempe, Arizona on January 3-6, 2006 and was attended by 40 national and international scientists from academia, national laboratories and industry. Graduate students and postdoctoral fellows also participated. The workshop provided a venue for direct interaction between researchers with expertise in diverse fields who use *in situ* TEM techniques to study synthesis processes, structure, properties and real-time evolution of nanomaterials. Workshop activities included scientific presentations, focused discussion groups, general discussion and report generation. The range of topics that was covered highlighted the capability of electron microscopy to probe the fundamentals of synthesis, structure and responsive chemical and physical properties of materials at the nanoscale by *in situ* dynamic observations. This workshop report is also available at the website: http://www.asu.edu/clas/csss/workshops/NSF_WS/

The main objectives of this workshop were to:

1. Share recent developments of *in situ* electron microscopy techniques and their applications to understand the behavior and properties of nanostructured systems such as catalysts, quantum dots, nanowires etc.
2. Identify high impact research topics that can be advanced by *in situ* techniques over a 10 to 15 year time span.
3. Identify those instrument developments that are needed to advance *in situ* nanocharacterization techniques.
4. Identify educational programs that will enhance societal awareness of the power of *in situ* microscopy for nanoscience and nanotechnology.

[†] In general, *in situ* studies, particularly of catalysts, tend to be conducted at pressures and temperatures that differ from real reaction conditions. The term *operandi* refers to those *in situ* studies that are conducted under actual reaction conditions.

Grand Challenges

Two clear grand challenges surfaced from the general discussions:

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1. **Expand *in situ* TEM into a Molecular Observatory for the synthesis and observation of active nanostructures.**

   Our understanding of synthesis and operation mechanisms tends to be limited by our inability to examine processes on the surface and interior of nanostructures. Incorporating additional characterization techniques into the *in situ* TEM will significantly expand the information about key stages of reactions and processes. Although a limited level of research effort is currently directed towards this goal, the capabilities of *in situ* TEM as a 'Molecular Observatory' for synthesis of active nanostructures is presently underexploited.

2. **Develop (ultra)fast image detectors to enable rapid observation of processes in active nanostructures at the atomic length scales.**

   The present time resolution of 1/60 sec is insufficient to observe dynamic intermediate structural and chemical changes occurring during the synthesis and operation of active nanostructures.

Advances within these grand challenges will have a profound influence on our ability to characterize active nanomaterials over the next 10 – 15 years.

Recommendations

To meet the above-mentioned grand challenges we make the following recommendations. The recommendations are drawn from the working group reports.

Catalysts and Nanomaterials for Energy, Environmental and Chemical Applications

- Develop the ability to analyze the products of catalytic reactions, localized to individual active sites and to simultaneously measure reaction products while observing structural changes on the catalyst. This is crucial for establishing structure-activity relationships.
- Develop imaging systems to make simultaneous *in situ* observations of the surface structure and overall morphology of supported metal clusters, (*e.g.* AFM combined with *in situ* TEM).
- Further develop spectroscopy techniques for high spatial resolution analysis of molecules on surfaces. This could be achieved using high-energy resolution EELS or by combining TEM with other spectroscopic probes such as Raman, IR and possibly EXAFS.
- Develop specimen holders for electrochemical measurements into the microscope chamber. This will enhance our understanding of electrocatalysis and electrochemical reactions.
- Incorporate computational modeling to support the interpretation of dynamic observations.

Nanomaterials for Information Technology

- Develop a quantitative understanding of the growth of composite structures, such as nanowires covered by dielectrics, and the relationship between structure and growth

conditions. This is important because, in principle, complete devices can be built in one nanostructure.

- Develop the tools to measure the effects of individual vacancies, kinks and surface steps on electronic transport properties. This goal could be greatly assisted by using aberration corrected TEM with 0.05 nm image resolution or better.
- Observe 'conventional' CMOS processing steps such as oxidation, diffusion, implantation etching etc., to identify the effect of chemistry and stress at an atomic level (HREM imaging combined with high spatial resolution spectroscopy). This becomes more important for 'post' CMOS processing due to the smaller scale of devices.
- Develop the capability to study the transport of spin polarized electrons as a function of sample heating, biasing and magnetization with high spatial resolution. Such measurements will assist in following spin polarization changes in spintronic materials.
- Develop models to understand the effect of temperature, electrical field and stress on the structure and properties of nanoscale components. This would be particularly valuable for the study of switching and fatigue in ferroelectric devices.

Nanoscale Processes in Structural Materials

- Develop methods for studying the dynamics of arrays of dislocations in response to applied stresses, with full characterization of all dislocation (Burgers) vectors in 3 dimensions. These studies are necessary to validate the substantial body of simulation work in the area of multi-scale modeling to predict mechanical behavior in materials.
- Dynamic imaging of dislocation cores at atomic level resolution during dislocation motion. The static structures of dislocation cores are just now being solved systematically with the latest aberration-corrected microscopes. While important, the understanding of static core structures yields only limited insight into core structures during propagation. Dislocation core structure evolution under applied stresses and heat is still relatively unexplored.
- Develop the ability to detect rapid changes in atomic structure at solid-liquid-gas interfaces, and to identify the role of impurity atoms and of external stimuli such as temperature, stress and applied fields.

Novel Tools and Facilities

- Create new mechanisms for providing access to facilities with a specific focus on *in situ* techniques. This can be achieved by establishing 'regional facilities' that specifically develop and operate *in situ* TEM based **molecular observatories** for a broad user base. Such facilities can follow the synchrotron model for funding and operation.
- Develop a high gas pressure environmental TEM to study the systems that can be studied under industrially relevant conditions at atomic resolution. Such an instrument will be used to monitor synthesis, operation and properties of catalysts, electronic and structural materials at the nanoscale.
- Develop an *in situ* equivalent of a diamond anvil cell for observation of nanoscale phase transformations of solids under uniform high pressure.
- Develop event detection software in order to maximize the data collection and analysis efficiency of rapid events that occur after a protracted latent nucleation period. This will be necessary once the grand challenge #2 of developing ultra-fast detectors is accomplished.

- Develop a reliable, high spatial resolution technique that can be used *in situ* to obtain quantitative information about the formation and distribution of point defects and adsorbates in active nanostructures.
- Integrate non-TEM-based techniques such as AFM, Raman, gas sensors etc… into the *in situ* TEM platform to collect additional information on the structure, chemistry, property relationship at the nanoscale.
- Develop accurate methods to measure local *in situ* conditions (*e.g.* pressure, temperature, field strength etc…).
- Develop methods for delivery and detection of photons in the near field in the TEM.
- Develop techniques to observe the materials response to neutron irradiation under reactor conditions.
- Develop robust first principle computational methods that can efficiently deal with systems of up to 1000 atoms.

Education, Outreach and Workforce Needs

- Undergraduate and graduate degree programs should include courses to teach nanoscience and technology. This can be achieved by (a) an integrated course taught by interdisciplinary teams, (b) courses organized around applications, (c) developing appropriate laboratory modules, (d) courses based on academia-industry liaison.
- Develop nanoscience summer courses for high school teachers (teacher enhancement) to make K-12 students aware of the future technologies.
- Develop educational modules and websites based on dynamic *in situ* TEM observations (including movies) for nanoscience and technology curricula.
- Organize special workshops to teach *in situ* TEM techniques and their applications.
- Develop remote teaching methods for advanced *in situ* electron microscopy as a part of nanoscience and nanotechnology curricula.
- Present research accomplishments at non-microscopy related conferences and symposia.
- Increase interaction between nanoscience research groups and local science museums and the media to facilitate public education on nanotechnology.

1 INTRODUCTION

There is a growing need for the development and characterization of active nanostructures where the system components may be functionalized to interact in a controlled manner with the ambient (pressure, fields, stress, heat…). Nanoscale evolution takes place during both the synthesis process and in response to external stimuli from the environment. For active nanostructures, understanding these dynamic changes is vital for developing new nanotechnologies. For example, understanding the relationship between nanostructure, reaction chemistry and kinetics is crucial for improving catalytic processes. Characterization of these complex transformations requires the use of advanced *in situ* methodologies so that the associated dynamic processes can be identified and understood. *In situ* transmission electron microscopy (TEM) is a natural tool to consider for the characterization of active nanostructures. Modern instruments possess a repertoire of imaging, diffraction and spectroscopy techniques

allowing nanostructure and chemistry to be determined with spatial resolutions better than 0.1 nm. Moreover, the range of ambient conditions that can be created *in situ* within the TEM has continued to expand and allows for variation in temperature, pressure, applied stress, electric or magnetic field strengths. The combination of high spatial resolution and varied ambient conditions makes *in situ* electron microscopy ideally suited to tackle the 21st century challenges of the nanoworld.

The potential impact of *in situ* electron microscopy on the development of nanoscience has not yet been fully realized. Although the history of making *in situ* observations is as old as the TEM technique [Butler and Hale, 1981], recent improvements in instrumentation have made it possible to obtain atomic level information under a variety of different ambient conditions [Gai, 1997, Microscopy and Microanalysis, 1998, Phil. Mag. 2004, Journal of Materials Research, 2005]. The advantages of these modern *in situ* techniques for nanoscience research include:

- Following the evolution of transformation mechanisms at the atomic-level, allowing different steps of the nucleation and growth processes to be identified from time resolved images and spectra.
- Identification of both stable and meta-stable intermediate phases.
- Determination of thermodynamic and kinetic data for individual nanostructures.
- Synthesis and structural characterization is performed simultaneously and this dynamic feedback may allow synthesis conditions to be rapidly optimized.

Scientific presentations during the workshop established the power of *in situ* TEM techniques for understanding dynamic physical and chemical processes at the nanometer scale, such as the melting behavior of nanoparticles, coalescence, phase transformation and crystallization. Some physical properties of nanomaterials, such as indentation effects, Young's modulus of individual carbon nanotubes, field emission and ballistic quantum conductance etc…, have also been measured using *in situ* TEM techniques.

As the number of research groups taking advantage of *in situ* TEM technologies is growing, it is important to evaluate the advantages and limitations of this approach in terms of different high impact areas of nanoscience. During this workshop three primary focus groups were established covering:

1. Catalysts and nanomaterials for energy and environmental applications,
2. Nanomaterials for Information Technology.
3. Nanoscale Processes in Structural Materials.

Most of the material included in this workshop report was provided by these three working groups. The report is structured to discuss the potential role of *in situ* TEM in each of the three primary areas. During the course of the workshop there was also discussion about necessary improvements in measurement techniques, such as data collection, data reduction, precise determination of temperature and pressure and incorporation of other techniques into the *in situ* TEM. Consequently one chapter is devoted to instrumental improvements that are necessary to maximize the impact of *in situ* techniques on nanoscience. Other areas of nanoscience outside the primary focus areas were also discussed at the workshop. These areas are briefly described in section 0 and were not covered in much depth but are recommended for further study. Finally, tools, facilities and education issues are covered in sections 6 and 7.
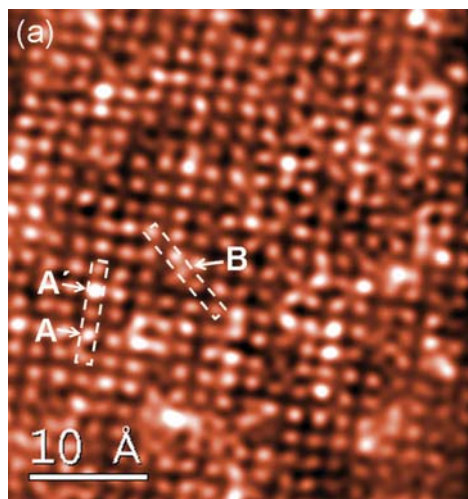
2 Catalysts and Nanomaterials for Energy, Environmental and Chemical Applications

The control of chemical transformations, is both an exceptional intellectual challenge and critically important for environmentally friendly production of energy and chemicals. In many applications, catalysis plays a central role and is integral to chemical processing and petroleum refining, emission control, energy production and transportation. Manipulation of catalytic materials at the nanoscale has long been, and continues to be, essential to the development and understanding of catalysts. Catalysis is a dynamic process, and information about catalyst morphology changes during reactions is critical for understanding and improving catalytic materials and processes at the nanoscale. Thus, many recent workshop reports [White and Bercaw, 2002, Davis and Tilley, 2003, Ray and Peden, 2005] have emphasized _the need for greatly improved methods for observing catalyst materials at the nanoscale as they are operating in a catalytic process._ ***A major goal for the characterization of catalysts is to follow molecular transformations on individual active sites in a catalytic reaction.*** This will require the ability to image the interaction of adsorbate molecules with the surfaces of catalytically relevant nanophase materials, and the measurement of reaction products from individual sites at technologically relevant temperatures and pressures.

2.1 Past Successes

Although there are many experimental methods to characterize catalytic materials and the catalytic process, TEM is unique in being able to provide real space images of industrially relevant high surface area catalysts at the atomic scale. It has been applied to many problems in catalysis and is the most frequently used technique to explore catalyst morphology and nano-chemical composition. The combination of atomic resolution imaging with nano-analysis provides important information on catalyst structure and composition at the nanometer level. This combination reveals subtle nanoscale heterogeneities that may be either undetectable or difficult to interpret with other approaches. Atomic resolution imaging has been extensively used to study many heterogeneous catalysts and is able to reveal particle, surface and defect structures, allowing a complete description of catalyst nanostructure. Z-contrast imaging has been particularly effective for locating heavy metal particles on light element supports – an extremely common combination in supported metal catalysts. High spatial resolution energy dispersive x-ray spectroscopy (EDX) and electron energy loss spectroscopy (EELS) have been extensively used to determine local composition especially in bimetallic catalysts.

Figure 1: Z-contrast image of La metal atoms on high surface area Al_2O_3 support (Wang et al, (2004) Nature Mat. 3, 143, Courtesy, A.Y. Borisevich).

It has long been realized that the state of a heterogeneous catalyst depends intimately on the ambient conditions (temperature, gas pressure, liquid composition etc…) encountered during
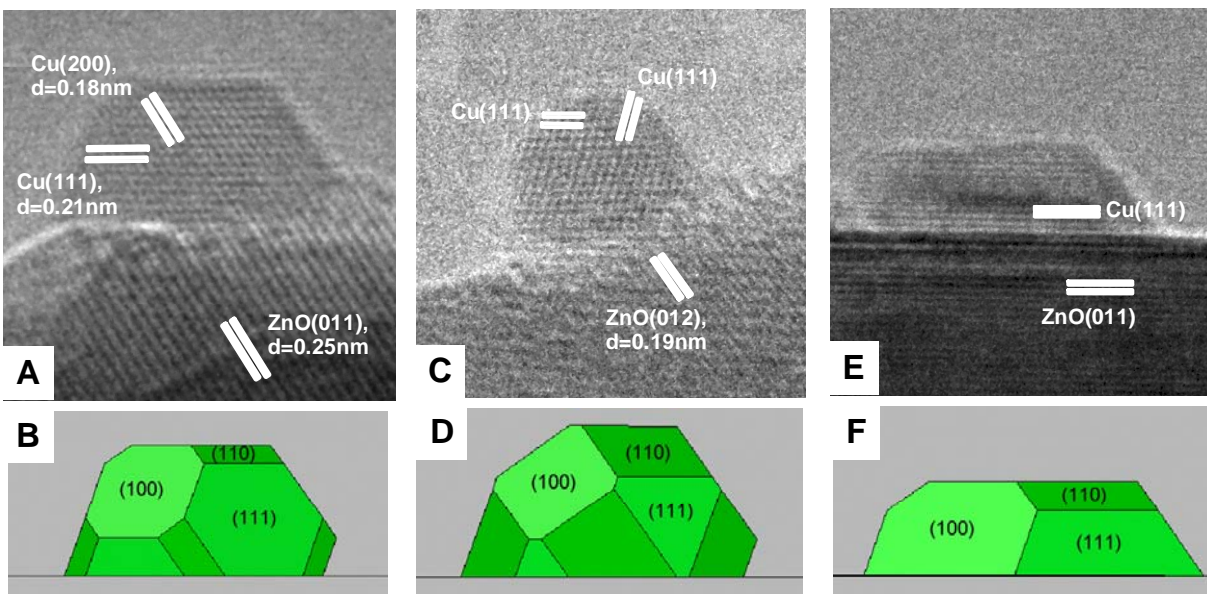
*Figure 2: Shape dynamics of Cu/ZnO catalyst in various gas environments. In situ HRTEM images and corresponding Wulff shapes in hydrogen (A,B), hydrogen/water (C,D) and hydrogen/carbon monoxide (E,F) at 220°C. (P. L. Hansen et al. Science **295**, 2053, 2002).*

catalytic operation. While many non-microscopy *in situ* techniques play a pivotal role in catalysis research, most of these techniques average information over areas far larger than the characteristic dimensions of the catalytically active nanostructures. However, the pioneering work of Baker, Gai and Doole *et al*. demonstrated that *in situ* environmental transmission electron microscopy (ETEM) can allow the structure and composition of active catalysts to be observed under reactive gas conditions down to atomic resolution [Baker, 1979, Doole *et al*, 1991 and Gai, 1999]. The impact of such instruments on catalytic research has been (and still is) restricted mainly because of the limited availability of ETEMs. Indeed for many years, most of the work on catalytic materials was performed by Baker or Gai's groups. This early work was able to demonstrate that very significant changes may take place in the structure and composition of active catalysts in reactive gas atmospheres at elevated temperatures.

2.2   Current Status

The need for sub-Angstrom resolution of functioning catalysts under reactive gas environments is contributing to the development of aberration corrected TEMs with large pole piece gaps. Correcting objective lens aberration is opening up new avenues for research on catalysis because it permits imaging to be perform at better than 0.1 nm and also permits light atoms like carbon and oxygen to be directly observed. The impact of this enhanced resolution on catalytic research is dramatically illustrated in Figure 1 where individual metal atoms can be clearly observed relative to atomic columns of an alumina support. *In situ* atomic resolution imaging permits dynamic changes in nanoparticle shape to be followed as a function of the reactive gas environment (Figure 2).

In addition to being able to directly determine nanoparticle sizes, shape and size distributions (all critical to catalyst activity), the TEM also permits the composition and distribution of the atomic species within the nanoparticles to be quantified. Moreover, nano-spectroscopy in the TEM allows the electronic interaction between the nanoparticles and the supports/adsorbates to be observed even when the interface is buried (Figure 3). This unique ability is critical to resolve the site specificity/selectivity of given reactions and therefore the future design of optimized catalysts.

Present-day *in situ* microscopes are able to combine atomic resolution imaging and nano-spectroscopy of catalysts at elevated temperature and pressures. The combination can follow all aspects of the genesis and evolution of the catalyst spanning synthesis, operation, de-activation and regeneration. The nucleation and growth of metal and bimetallic nanoparticles can be followed during catalyst synthesis. Dynamic changes in nanoparticle morphology during catalytic reactions can be followed at video rates (see Figure 4) providing new insights into the underlying reaction mechanism. Combining *in situ* nano-spectroscopy with imaging offers the promise of correlating variations in the activity of nanoparticles with their structure and chemistry. Catalyst de-activation and regeneration processes can also be studied under reactive gas conditions.
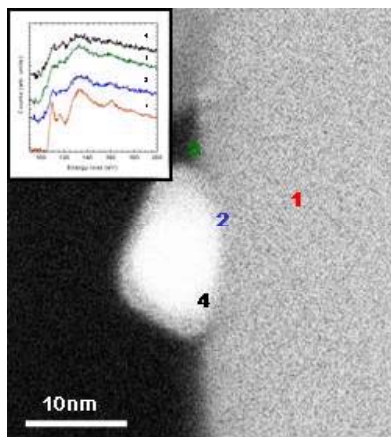
Figure 3: *Z-contrast image of a Pt nanoparticle on the surface of SiO$_2$ at 300°C in the microscope vacuum. Insert: Silicon L-edge spectra show a preferential reduction of the support in the region of the nanoparticle (Klie et al, J. Catalysis* **205**, *1-6 (2002)).*

2.3 Future Challenges

2.3.1 Fundamental Questions and Current Barriers/Challenges

Despite these successes, the current generation of instruments suffers from significant limitations on pressure, time resolution and temperature. Moreover, for catalytic research it would be advantageous to incorporate additional surface imaging and spectroscopy techniques into the *in situ* TEM. Some of the current challenges and barriers are listed below.

Surface structures:

Insight into nanoparticle shapes and exposed surface sites is important for micro-kinetic modeling. Since nanoparticles adapt to their working environment, such information needs to be obtained under reaction conditions. The development of methods to simultaneously image and analyze surface structures and adsorbates on individual nanoparticles is essential. For example, this could be achieved by integrating a scanning probe microscope (SPM) into the TEM or conceivably through robust diffraction reconstruction methods.

At the present time, EELS is being used to observe adsorbates of 1–2 monolayers on the surfaces of nanoparticles. In future, the sensitivity of EELS needs to be improved to allow individual molecules to be detected. Improvements in energy resolution will allow both the vibrational spectrum and electronic structure of adsorbates on the active sites of nanoparticle surfaces to be determined. Other spectroscopic probes, such as Raman, IR and even possibly EXAFS, in conjunction with TEM would also provide unique insights.
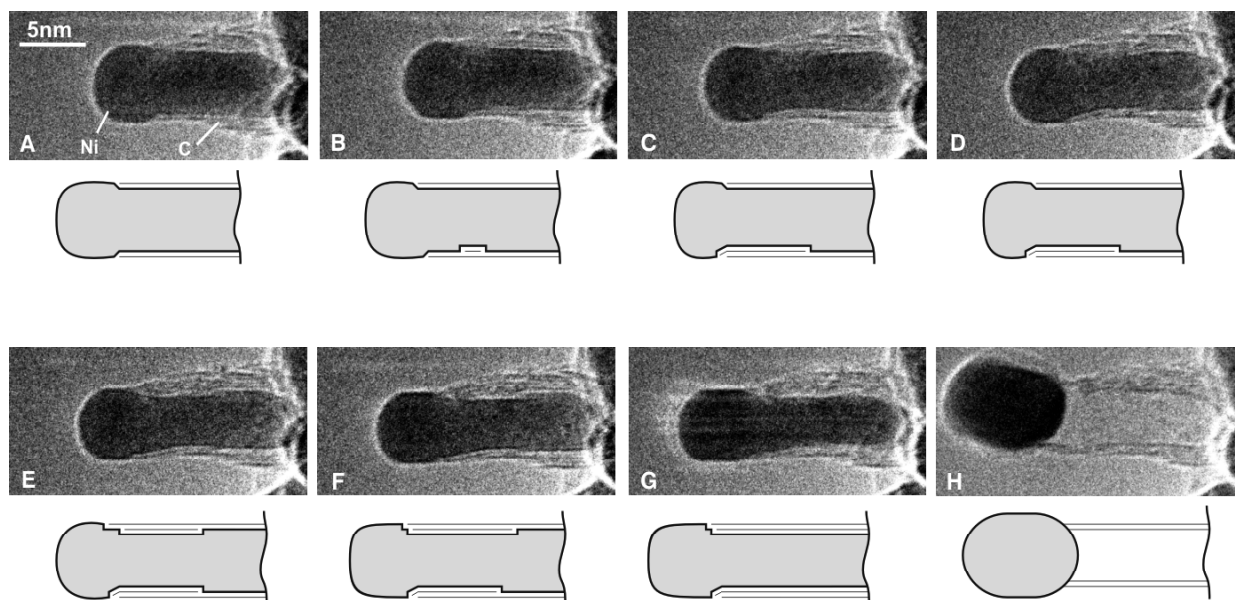
Figure 4: *Image sequence showing the growth of multiwalled carbon nanofiber. The drawings are included to guide the eye in locating the monoatomic Ni step edges which are the active sites for growth. (Reference: S. Helveg et al. Nature **427**, 426 (2004)).*

Correlating nanostructure with reaction products:

Correlating observed nanostructures and compositions with simultaneous measurements of reaction products is crucial for establishing unambiguous structure-activity relationships. At present, measuring reaction products seems to be a daunting task as the amount of catalyst used for TEM is significantly smaller than the surrounding heated mass in contact with the gas phase. *In situ* cells that better-confine the gas phase around the specimen will be needed to allow other probes to access the catalyst surface. In this respect, it should be noted that *in situ* HRTEM investigations presently are carried out at modest pressures (10 mbar) hence *in situ* cells capable of operating at higher pressures, *e.g.* 1 bar, would be an important development for catalysis research. The ability to analyze the products of catalytic reactions, localized to individual sites, would represent a significant advance in catalyst characterization tools. This could be achieved through ultrafast electron diffraction, localized mass spectrometry or some other form of "nano-sniffer".

Bimetallic nanocatalysts:

Bimetallic and multimetallic nanoparticles possess unique active sites due to either geometric ensemble effects or due to special electronic effects. Proper development of bimetallic/multimetallic nanocatalysts will have tremendous economic impact in many areas of catalysis. Key issues relate to intimate and uniform intermixing such as surface segregation of nanoparticles under various gas environments, and compositional variations within individual nanoparticles. Our present inability to observe the surface structure of these nanoparticles is a major barrier.

Imaging of light-elements and anions:

TEM images are presently able to provide accurate locations of the heavy elements, usually the cation. However, oxides, sulfides and carbides possess unique catalytic properties, which are attributed to the anionic and light-element sub-lattices, defects and their gas-induced dynamic changes. Direct insight into the local geometric configurations of the light-elements as well as their local electronic properties is needed to better establish structure-activity relationships in these systems. This will require aberration-corrected *in situ* electron microscopy and spectroscopy.

Promoters:

The introduction of low concentration promoter species can often boost catalytic activity and selectivity, as well as stability. To understand the functionality of the promoters, insight about the spatial distribution in the catalyst, even with low concentration, is important. *In situ,* single-atom, spectroscopically-resolved, TEM imaging will be important for detecting how these promoters are distributed during catalyst activation and their location with respect to the catalytic active sites.

Deactivation mechanisms:

A major problem in the industrial application of catalysis is the long term degradation of catalytic performance, caused by processes such as poisoning, coking and sintering. Detailed insight into the underlying atomic-scale dynamic processes is essential for designing catalysts with improved stability. This knowledge is often difficult to acquire by indirect methods, but *in situ* TEM can provide a direct view. Specifically, this will require improved resolution to detect adsorbed atoms on a support, and dynamic recording with drift correction to observe events as a catalyst is exposed to varying temperatures in a gas environment.

Synthesis of Nanostructured Catalysts:

A key requirement for meeting the grand challenge of catalysis is the development of stable catalysts containing nanoparticles of uniform size, composition, and surface structure. This will require very careful control of the preparation methods for synthesis of the trillions of nanoparticles that carry out the reaction in a typical industrial catalytic reactor. *In situ* techniques can be used to follow the fundamental process that is taking place during catalyst synthesis in order to develop new approaches to catalyst fabrication.

2.3.2 Potential High Impact Research Areas

We highlight below some of the application areas that would benefit from the development of advanced *in situ* electron microscopes and image analysis techniques.

Synthesis of Supported Metal Catalysts

The effectiveness of a catalyst depends on its ability to create and maintain a large number of active sites for the catalytic reaction of interest. The current generation of supported metal catalysts consists of particles of differing size and shape with a concomitant wide distribution of surface sites. To achieve the goals of "catalysis by design", we must be able to precisely control the nucleation and growth of metal nanoparticles on high surface area supports

to give well-defined distribution of active sites under reactor conditions. As such, we require catalyst synthesis methods that provide a narrow distribution of sites and their coordination with their neighbors. Mesoporous materials, prepared via self-assembly of surfactants, are ideal 'scaffolds' to support nanoparticles. Understanding and controlling the synthesis of metals and oxides sites on these mesoporous materials represents an exciting challenge for the preparation of model, uniform active catalyst structures for fundamental studies of catalytic materials and processes.

Impregnation techniques play a major role in catalyst synthesis, but little is known about the role of nanoscale surface features on the self-assembly process. The distribution of surface defects and facets on the support will strongly influence the drying, decomposition, diffusion, nucleation and growth mechanisms taking place during the catalyst synthesis processes. *In situ* environmental electron microscopy can be used to provide exciting new insights into the nanoscale processes controlling catalyst synthesis and activation (see Figure 5).

Catalyst Sintering and Deactivation

In situ microscopy can help address a problem that pervades many applications of heterogeneous catalysts, namely the loss of active surface area during high temperature operation. Catalyst sintering represents one of the most important factors limiting their long-term durability. While nano-sized metal particles represent the mainstay of heterogeneous catalysis, coarsening of nanoparticles can occur at rather modest temperatures, causing irreversible changes in activity and selectivity. Industrial catalytic processes must therefore operate at temperatures where the rate of metal surface area loss due to sintering can be kept within manageable proportions. Despite its obvious technological importance, fundamental understanding of sintering is still lacking and predictive models are not available. A major unknown is the mechanism of catalyst sintering. Does it involve migration of atoms – ripening, or migration and coalescence of nanoparticles – dynamic coalescence? *In situ* TEM provides the ability to follow the evolution of the shape, size and location of individual nanoparticles as they are used in a catalytic reactor. Operational limitations may restrict the temperature and pressures available for the study of these phenomena, but judicious choice of operating conditions will allow mapping of individual events that will critically impact our understanding of catalyst stability.

Figure 5: In situ nucleation of Ni nanoparticle on high surface area titania support (P25). Left panel shows $Ni(NO_3)_2$ precursor (arrowed) covering an anatase grain. Right panel is same area showing growing Ni nanoparticle nucleating and growing during in situ reduction at 350°C in 1 Torr of CO. (Li et al, J.Phys. Chem B, 109, 13883).

Development of Alternative Fuels (Gas to Liquid and Coal to Liquid)

Processes to convert natural gas and coal to liquid fuels are currently under development in industry,

and they are based on cobalt and iron catalysts due to their high activity. The nature of the active phase in Fe catalysts still remains a subject of intense debate despite the fact that over 70 years have passed since the discovery of this process by Fischer and Tropsch (F-T). Presently, these catalysts are used for conversion of coal-derived syngas where the H_2/CO ratio is around 0.7. The high water gas shift activity of the Fe makes it possible to operate with an H_2/CO utilization ratio that matches that of the incoming feed. Activation conditions (H_2, CO or syngas) are known to profoundly affect the reactivity of the final catalyst. However, it has been notoriously difficult to correlate catalyst reactivity with average catalyst composition. Therefore, the consensus has been to associate catalyst reactivity with a surface phase that is difficult to characterize [Huang et al, 1993]. Surprisingly, while magnetite is known to be unreactive for the F-T synthesis, surface analysis by XPS reveals magnetite as the only observable phase [Kuivila et al, 1989]. Such observations apparently confirm the difficulty of correlating reactivity with catalyst structure, and possibly impede progress in the design of improved catalysts. Better understanding of these Fe catalysts will be critical as we begin to deploy our coal reserves for conversion to liquid fuels. There are also a number of unresolved issues with respect to Co-based catalysts, namely the oxidation of nanosized particles leading to deactivation, and the mechanisms of sintering that may also lead to catalyst deactivation. In each of these catalyst systems, it is important to perform observations as close as possible to operating conditions. The Fe and Co phases are air sensitive, and the transfer from a reactor to the microscope can lead to irreversible changes. Furthermore, there are large amounts of interstitial carbonaceous species that can precipitate when the sample is cooled. Observations carried out *in situ* will be necessary to identify the active phase of the catalyst, and to explore the de-activation mechanisms.

Hydrogen Production from Renewable Feedstocks

Chemicals produced from biomass or corn, such as alcohols, have the potential to serve as an important renewable source of energy and may help to reduce our dependence on dwindling foreign and domestic oil supplies. Methanol and ethanol are particularly promising energy sources since they can be reformed to produce hydrogen, which can then be used in fuel cells for producing electricity. Ethylene glycol is a byproduct of bio diesel production and may soon be available in large quantities. It is necessary to develop novel catalysts that are selective for these conversions. Examples of catalysts suitable for these processes include ZnO-supported Co or Pd. In the case of Pd/ZnO it is found that the catalyst must be pretreated to attain the highest selectivity for H_2 production and to minimize the formation of unwanted CO. It is desirable to know which surface structures are formed under specific pretreatment conditions. *In situ* TEM provides the spatial resolution to determine the shapes, exposed surface facets and compositional heterogeneity in these bimetallic catalysts. However, new methods will need to be developed to map out the surface structures on these nanoparticles under reaction conditions.

Photocatalysis

Catalytic production of hydrogen by electrolysis of water, initiated by ultraviolet (UV) light (Honda-Fujishima effect), shows significant promise for providing a solution to our energy needs. The exact role of titania in this process is still not well understood and is a subject of intense research. Moreover there is also a need to increase the sensitivity of photocatalytic materials to visible light, rather than the UV spectral region, in order to effectively utilize the energy provided by the sun. Recently, much progress has been realized in many research institutes by the addition of sulfur and/or nitrogen dopants to titania-related compounds.

However, the mechanism for the broader spectral response is still unknown. Critical questions remain unanswered concerning the location of dopant species, their influence on electronic structure, interaction between titania, water vapor and oxygen, and the nature of the active surface sites.

Recently, a fiber optic has been incorporated into the sample stage of a HREM with an environmental cell [Yoshida et al, 2004], allowing for *in situ* electron microscopy of photocatalytic processes. This work demonstrates that *in situ* techniques can be used to study the nanoscale processing taking place in active photocatalytic materials. This approach can be expanded to include other optical characterization techniques such as UV spectroscopy and vibration spectroscopy. Incorporation of ultrafast techniques may allow photon induced transitional states to be probed with high spatial and temporal resolution.
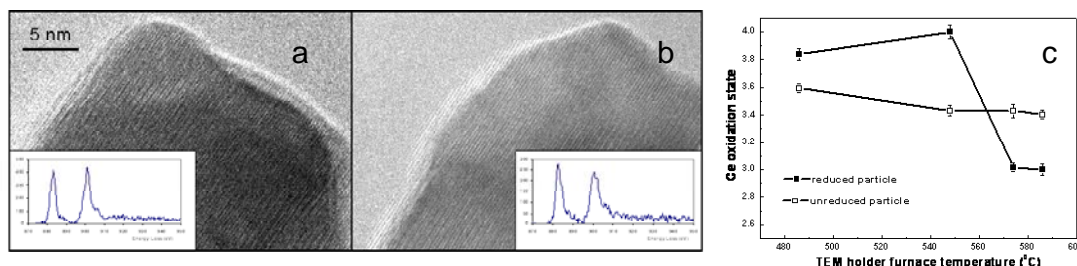
Figure 6: *In situ HREM images from nominally identical nanoparticles of $Ce_{0.5}Zr_{0.5}O_2$ recorded at 575^oC in 1 Torr of H_2. The in situ EELS (inserts) show that the particle b) is more strongly reduced and active than the particle a). c) Oxidation state for same two particles as a function of temperature (Courtesy R. Wang).*

Environmental Catalysis

Catalytic processes for environmental protection are well known for bringing us clean air and water. Catalytic emission control technologies have also reduced air and terrestrial pollution from large-scale industrial power plants, as well as chemical and petroleum production facilities. Increasing demands for energy by the developing world mean that catalytic emission control will remain an active and critically important area of research. To identify some of the challenges in this area, we focus specifically on the needs for new and improved catalytic emission control technologies for the removal of nitrogen oxides (NO_x). However, many of the general scientific and technological questions also apply to many other areas of catalytic emission control for environmental protection.

While three-way catalysis (TWC) is considered a mature technique, improvements are still sought, such as reducing the amount of expensive precious metals in the formulations, protecting these catalytically active materials from deactivation, and improving the oxygen-storage material (currently ceria-zirconia). *In situ* electron microscopy can play a critical role in exploring the response of these catalysts to oxidizing and reducing conditions (see Fig. 6).

Operating internal combustion engines under net oxidizing conditions is highly desirable to increase fuel efficiency. However, this mode of operation, for example in diesel engines, makes traditional TWCs ineffective for the reduction of NO_x in the exhaust gas stream. The major challenge is to efficiently remove NO_x species in the presence of excess oxygen. In the last decade or so, a number of new approaches toward NO_x reduction in oxygen-rich environments have been explored [Heck and Farrauto, 2002]. Two of the leading technologies for this application are selective catalytic reduction (SCR) with urea and lean NO_x traps. To successfully implement these new 'lean NO_x' technologies, it will be necessary to develop improved and optimum materials by, for example:

- Understanding the chemical and physical nature of the active catalytic species, especially in the new catalysts being used in these technologies, such as vanadia or tungsten oxide supported on titania, and Pt-BaO/alumina;
- Determining the location of promoter species in order to establish their role in enhancing catalytic performance;
- In the case of lean NO_x traps, significant morphological changes continually take place during operation. Understanding how these changes depend on operating conditions is critical to developing optimum materials.

In situ electron microscopy can make a significant contribution in this area by helping to elucidate the structure, chemistry and dynamic changes taking place under reactive gas conditions.
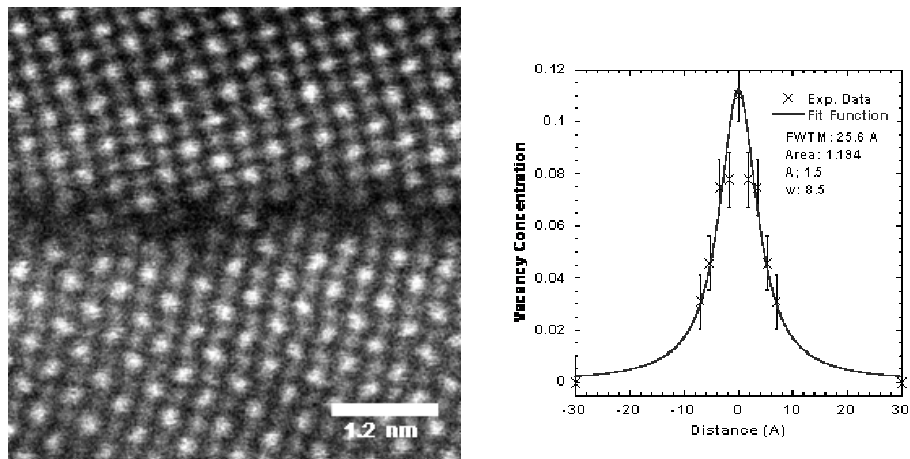
Figure 7: (a) atomic resolution image of a high-angle grain boundary in SrTiO₃. (b) From the integrated Oxygen K-edges a vacancy profile at the grain boundary can be formed. This vacancy profile leads to a charged grain boundary and a barrier to both ionic and electronic conductivity. (Courtesy N. Browning).

Solid Oxide Fuel Cells

In principle, solid oxide fuel cells (SOFC) are the most efficient method for converting chemical energy into electrical energy. A major goal in this area is to develop devices that can run over extended time directly on hydrocarbon fuels without the need for a separate reformer. This requires the development of suitable anode and cathode catalysts and electrolytes with desirable low temperature oxygen conductivities. A major challenge is to maximize the performance of the anode/cathode materials (and associated electrocatalyst) under strong reducing/oxidizing conditions. *In situ* electron microscopy can provide direct information on the dynamic nanostructural transformation processes taking place at elevated pressure under reactive gas conditions. This will allow the underlying nanoscale processes such as interfacial reactions, carbon formation and vacancy migration and segregation to be studied. For example, clustering, ordering and segregation of vacancies to extended defects leads to reduced conductivity while the segregation to component interfaces leads to debonding and structural instabilities. The unique ability of the TEM to characterize the presence of the extended defects, the vacancy distribution and the electronic state of the component atoms, provides a way to analyze defects and interface engineering to optimize the conductivity vs. stability of the fuel cells (Figure 7).

Studying fuel cell components under both reactive gas and electrical biasing conditions would be extremely desirable to understand ion transport and other reactions that taking place.

Development of Proton Exchange Membrane Fuel Cell Catalysts

One of the major obstacles to the commercialization of proton exchange membrane (PEM) fuel cells is the need for desirable electrode catalysts. The current Pt-based catalysts are expensive and are susceptible to poisoning by CO and other impurities leading to rapid deactivation. Development of bimetallic catalysts, such as PtRu, PtMo for the anode and PtCr, PtCo for the cathode, and non-noble-metal based catalysts, can address some of the critical issues facing the commercialization of PEM fuel cells (see Figure 8).

Environmental TEM can have a significant impact on the development of PEM fuel cell catalysts by examining, *in situ*, the particle size distribution, the composition of the individual nanoparticles, the spatial distribution of the nanoparticles with respect to the support, the shape of the nanoparticles, and most importantly the surface segregation of bimetallic or multimetallic nanoparticles. It can also be used to study the dynamic evolution of the individual nanoparticles under near-working conditions to understand the deactivation mechanisms of both the anode and the cathode catalysts. Insights from such ETEM studies can be used to develop new catalysts, or to optimize existing catalysts, to obtain more robust, stable, and highly active electrodes. Development and incorporation of micro devices for electrochemical measurements into the microscope chamber will significantly enhance our understanding of electrocatalysis and electrochemical reactions. The technology developed for this study can be applied to study the synthesis-structure-performance relationships of nanostructured catalysts used in liquid catalysis.
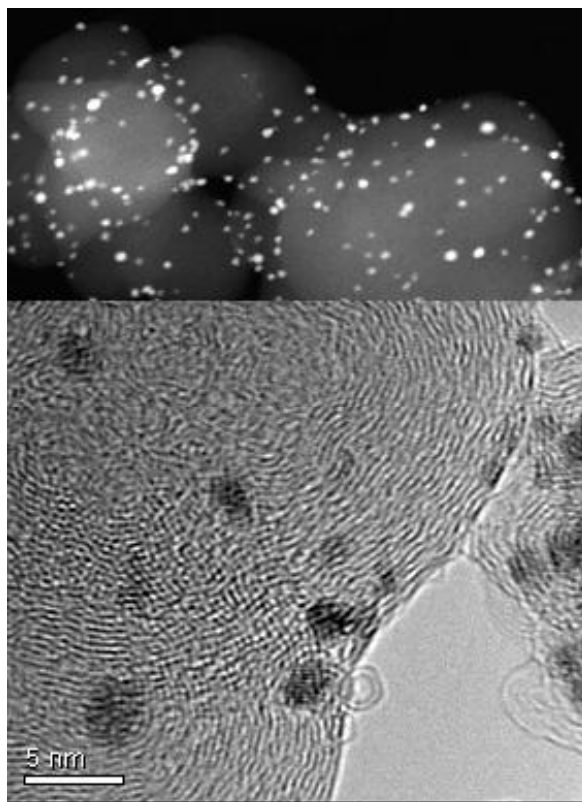
Figure 8: High-angle annular dark-field image (top) the size and spatial distribution of the catalytic nanoparticles supported on granular carbon support and high resolution TEM image of a PEM fuel cell catalyst showing of the same catalyst showing atomic and nanoscale structural information (Courtesy Jingyue Liu).

Batteries

High capacity lightweight rechargeable batteries are essential for the large range of portable electronic devices that we have come to accept as an essential part of the modern world. Batteries with increased charge storage per unit weight would revolutionize transportation, initially being used in hybrid electric vehicles. Lithium is the charge carrier for batteries used in portable electronic devices, and the anode and cathodes potentially are able to accommodate

large amounts of lithium without changing phase. The lithium should also be able to move easily under an applied electric field. The present generation of Li batteries (sometimes called Li ion batteries) use layered compounds, graphite for the anode and layered transition metal oxides for the cathode. In the search for new materials it is very useful to study the structure of both anode and cathode while the battery is being cycled to see if there are any phase changes as the Li intercalates or deintercalates. Most current structural studies involve *in situ* XRD since (a) Li is difficult to image using TEM, and (b) Li deintercalates very quickly due to electron beam interactions in the microscope vacuum. However, some model intercalation and de-intercalation reactions have been studied using TEM with NH_4^+ or Hg^0 ions instead of Li. Many of the issues with some of the newer materials such as $LiFePO_4$ involve changes in nanostructured phases. Imaging of structural changes associated with the charge and discharge process would be very useful in the design of new materials.

Small electrochemical battery cells whose components can be imaged in the TEM while the battery is cycled have already been proposed. Such devices would be of great help in understanding the behavior of the nanophases during cycling. It would be an added bonus if the distribution of Li can be mapped during cycling to investigate possible charge carrier transport problems, and to resolve the many outstanding issues about what happens at the solid electrolyte interface for both cathodes and anodes.

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3   Nanomaterials for Information Technology

As the size of devices used for electronic, optical and magnetic applications is continuing to shrink, the demand for fabricating nanoscale components has increased dramatically. The 'nanoworld' has now become the 'real world' for many of these technologies. High-resolution imaging and analytical techniques, such as TEM have become essential tools for characterization. Traditionally, *ex situ* synthesis followed by characterization and property measurement has been the way to establish structure-property relations. However, there have always been questions about the specific role of defects, dislocations, grain boundaries etc. in controlling electronic, optical and magnetic properties of nanomaterials. Some of these questions are now being answered by simultaneous measurement of properties and nanoscale structure using *in situ* transmission electron microscopy techniques.
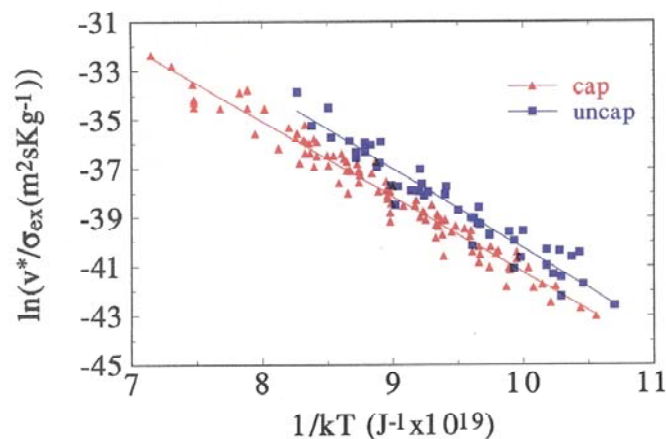
Figure 9*: Annealing of metastable strained (Si)/Ge$_x$Si$_{1-x}$/Si films in situ in the TEM allows misfit dislocation propagation to be directly observed and quantified. This enables strain relaxation dynamics to be quantified in this system, and also provides insight into fundamental dislocation mechanisms such as the energetics of kink nucleation and growth. The figure shows universal curves for extensive sets of measurements of dislocation glide velocities in Ge$_x$Si$_{1-x}$/Si(100) ("uncap") and Si/Ge$_x$Si$_{1-x}$/Si(100) ("cap") structures, where each measured velocity is normalized to an equivalent velocity of 1 Pa in pure Si. (Hull and Bean, (1992) Phys. Stat. Sol. (A) 138, 533).*

3.1   Past successes

In situ TEM has made major enabling contributions to understanding, and solving, the materials issues associated with the relentless increase of the performance levels in the information technology industry. This advance is based primarily upon the continuous shrinking of device dimensions and the introduction of new materials, which in turn has brought an incessant stream of new materials challenges. While addressing these challenges has employed an extensive array of experimental and modeling techniques, *in situ* TEM has made many key contributions, including fundamental understandings of phase transformations in thin films and restricted volumes, oxidation, electromigration, dislocation injection in heteroepitaxy and electroplating.

In situ transmission electron microscopy has also made widespread and key contributions to understanding extended defect dynamics in semiconductor materials. For example, full kinetic descriptions of the dynamics of dislocation injection into lattice-mismatched heteroepitaxial
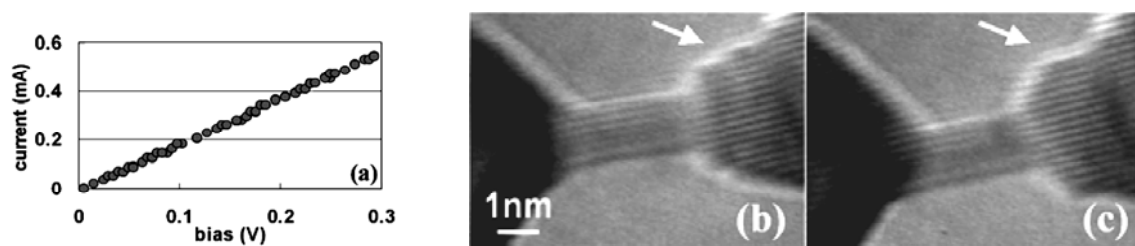
Figure 10 (a) A typical example of a linear I-V curve. (b-c) Corresponding TEM images taken at 0 V (b) and at 0.26 V (c) obtained *when the bias voltage (0<V<0.3 V) was increased. as the electrodes approached each other, the width of the short nanowire increased, causing nonlinear I-V curves. On the other hand, linear I-V curves were observed for a long nanowire, because the width did not change* with increasing bias voltages *(Yoshida et al, (2005) Appl. Phys. Lett. 87 103104).*

films (Figure 9) have helped define the growth and processing conditions for integration of strained epitaxial films into electronic devices. In particular, incorporation of heteroepitaxial Ge_xSi_{1-x} films into conventional Si-based technology have greatly improved device technologies for both bipolar and CMOS devices. The precisely defined geometry and stress states in these *in situ* experiments have also allowed fundamental microscopic mechanisms of dislocation propagation, such as kink nucleation and growth, to be examined and quantified.

During the past decade, steady progress has been made towards understanding the synthesis and properties of electronic materials. Real-time studies of ion etching, ion implantation, and dopant activation are now feasible. It is important to understand the evolution of stresses in the structure, which can reach 1 GPa or more. Such stresses can be monitored by quantitative electron diffraction techniques, or conceivably by integrated near-field Raman measurements. The combinations of these two techniques would offer the spatial resolution and stress sensitivity necessary for future CMOS generations until the end of the roadmap.

One of the most important developments during the last few years has been the ability to combine property measurement with structural and/or chemical analysis. For example, the structural changes and *I-V* curves for gold quantum point contacts (QPCs) were simultaneously measured and observed by UHV transmission electron microscopy (TEM). A scanning tunneling microscope (STM) system in the TEM at room temperature was employed to fabricate the gold QPC. (Figure10). The results from these measurements suggest that the observed conductance increases because of a thickening of the contact area. It was also confirmed that changing the applied bias voltage could control the thickening process.

Development of an electrochemical cell incorporated into a TEM holder has enabled researchers to understand the effect of electrical current on the nucleation and growth of electroplated films with good spatial and temporal resolution (Figure 11).
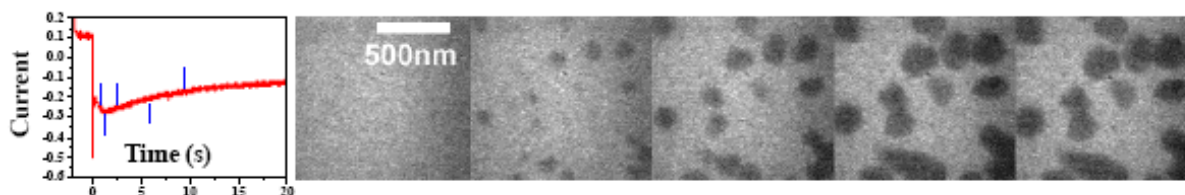
Figure 11. *Current vs. time for electrochemical deposition of copper nanoclusters on Au, combined with stills extracted from a video recorded simultaneously showing nucleation and growth of copper clusters. The times corresponding to the stills are indicated by blue tick marks. (Radisic et al., Nanoletters 6, (2006)238-242).*

3.2   Current Status

Synthesis of Nanostructures

In order to optimize the synthesis conditions for active nanomaterials such as quantum dots, quantum point contacts, nanowires and nanotubes for selective applications, a quantitative understanding of the relationship between structure and growth conditions is required. It will be particularly important to calibrate the growth conditions, such as obtaining an accurate measurement of local sample temperature. Similarly, pressure gauges or measurement of flux and gas composition during growth should be calibrated using known systems.

Other applications, such as quantum cellular automata structures, require the placement of nanoscale islands formed by self assembly to be controlled. *In situ* TEM can contribute to an understanding of spatial control during self-assembly. For example, patterning of the substrate surface by low dose FIB irradiation followed by annealing creates small pits one plane deep that act as preferential sites for the nucleation of quantum dots during deposition. Other self-assembly processes have been understood through *in situ* analysis.

Single electron devices require fabrication of nanometer sized structures for a number of applications in nanotechnology. As sub-nanometer sized electron beam diameters are now routinely attainable, direct placement techniques can also be employed to fabricate nanostructures. In electron beam induced deposition (EBID), a focused electron beam is employed to locally dissociate a gaseous precursor directly on the substrate. Simple or more complex structures can be deposited depending on the substrate and deposition conditions, as demonstrated, for example, by Furuya's group. The development of multiple beam systems may make this approach extremely valuable for maskless lithography in the future. It may also be feasible to use this approach to locate catalytically active nanoparticles at well-defined positions in space. There are still many fundamental questions associated with high resolution EBID. *In situ* electron microscopy will play a critical role for exploring the dependence of the deposition rate, structure and composition as a function of deposition conditions.

Nanowires of Si and Ge can be grown catalytically. The effects of different gas environments have been directly related to the structure of individual wires. Further experiments of this type could be done on other materials. Examples include electrode materials, dielectrics, and new materials such as organic nanostructures.

Scientific interest in carbon nanotubes (CNTs) stems from their electronic, mechanical and chemical properties that arise from their structural and morphological variations. Thus, the critical issue in all nanotube applications, from the macroscopic to the nanoscale, is the ability to control their fabrication and growth. *In situ* TEM observations are expected to make significant contributions for the optimization of the growth conditions tailored for given properties and applications. Recent *in situ* observations of CNT growth processes confirm the feasibility of the approach (Helveg et al 2004, Sharma and Iqbal 2004, Banhart et al 1999).

Size effects in ferroelectric nanostructures

The application of *in situ* TEM to the study of ferroelectric materials has been limited mostly to heating experiments. The Curie temperature has been directly observed by *in situ* heating experiments and the transition is indicated by the nucleation and growth of ferroelectric domains with spatial resolution on the order of 10 nm. *In situ* TEM has also been used to detect the ordering of oxygen octahedra tilting and the ordering of antiparallel ionic displacements. Preliminary reports of low-temperature ferrielectric-ferroelectric phase transitions, using a

cryogenic stage, indicate that it is feasible to make dynamic observation of the process. The application of *in situ* methods to study the ferroelectric behavior needs to be further developed.

Electric fields have also been applied to insulating ferroelectric materials, but results tend to be at low spatial resolution because of sample thickness effects and because of instabilities leading to image drift. Ferroelectric domain growth and electric field-induced grain-boundary/domain-wall fracture have been directly observed. Recently, *in situ* TEM has been applied to antiferroelectric ceramics to monitor the electric field-induced transformation of the incommensurate phase [He and Tan, 2005].

Ferroelectric nanostructures can be fabricated either in the TEM chamber or outside. The *in situ* TEM technique can make unique contributions by allowing measurement of local area polarization-field hysteresis loops and dielectric permittivity. Combined with direct ionic displacement mapping, it would establish the size dependence of electric/dielectric/ferroelectric properties.

Dopant distribution and migration

There is a pressing need for the development of a reliable, high spatial resolution technique that can be used to obtain quantitative information about dopant distributions in semiconductors, both for the evaluation of process parameters and to provide input to simulations of dopant diffusion. Off-axis electron holography offers the potential to provide such information. One of the most exciting developments is the application of electron holography, together with electron tomography, to provide three-dimensional information about electrostatic fields in materials with a spatial resolution of ~1 nm in all three directions.

Electronic properties

As electronic devices become increasingly smaller, the need to discover novel electronic nanomaterials becomes imperative. Fundamental understanding of electronic transport in increasingly small materials is essential to the design of nano-devices. The scanning tunneling microscope (STM) probes the electronic properties of the surface, and TEM probes microstructure. Hence, novel designs of hybrid TEM-STM sample holders provide a creative method to explore site-specific electronic transport properties of nanomaterials.

Another challenge is to isolate specific defects at the atomic scale, such as vacancies, kinks or surface steps, and measure their effect on the electronic transport properties. Again, the ability of an *in situ* TEM-STM combination to locate nanostructures, characterize changes in structure and chemistry, and probe electronic transport properties during dynamic processes is unique. These observations are consistent with the existence of localized, on-tube nanodevices as theoretically predicted for point defects in individual carbon nanotubes.

As another example, the oxygen vacancy is speculated to pin ferroelectric domain walls and lead to electric fatigue in oxide semiconductors. In this case, directly imaging oxygen vacancies and their interactions with moving domain walls/phase interfaces is highly desired. This may be achieved using aberration corrected ETEM, where oxygen partial pressure can be controlled, to image and *in situ* engineer/manipulate oxygen vacancies.

Electrical Properties of Single dislocations

The detailed calibrations between misfit dislocation velocity and film stress have enabled the propagation velocity of a dislocation to be used as a measure of local stress, for example during interactions of dislocations with point defect atmospheres and with each other. Injection

of dislocations into Ge_xSi_{1-x}/Si p-n junctions has been directly correlated to reverse-biased generation currents, and in the near future experiments determining the electrical properties of single dislocations will be feasible by *in situ* TEM. This leads to the possibility that improved understanding and control of dislocations could lead to their use as active nanoelectronic device elements.

3.3 Future challenges

Information Technology is currently part of a thriving industry, complete with a roadmap laid out by Moore's law. This roadmap essentially demands the development of smaller nanoscale functioning devices and the future challenges are driven by this technological need.

3.3.1 Fundamental Questions and Current Challenges

Microelectronics Materials

There are two important issues that are crucial to advance the applications of microelectronic materials:
- How can we improve existing materials to enable the current scaling of microelectronic devices to continue?
- Can new functional materials and structures be developed for the "post" CMOS world?

Over the ten-year timeframe, the design of microelectronic circuits will undergo significant changes. These will be driven partly by the increased difficulty of applying conventional techniques (lithography, etching, doping, etc.) to smaller features, and partly by the increased need for understanding, and hence controlling, the growth of nanostructures and nanostructured materials. The ultimate aim is to obtain appropriate control of the growth, so that the electronic and structural properties of these nanomaterials can be defined well enough to use them as components in manufacturable circuits. This aim is close to being achieved for many types of nanostructure, such as nanotubes, nanowires and quantum dots but not for electrode materials and dielectrics, and new materials such as organic nanostructures. The growth of composite structures, such as nanowires covered by dielectrics, are particularly important as it provides means to build complete devices in one nanostructure.

An intriguing possibility is the *in situ* processing of nanostructures in order to prevent any air exposure or the need to make a TEM sample by removing the nanostructure from its substrate. For example, a carbon nanotube emitter can be fabricated by *in situ* transmission electron microscopy methods (1): An amorphous carbon nanopillar that can be fabricated by electron-beam induced deposition in ETEM; the obtained amorphous carbon nanopillar can be catalyzed to form an individual tube. (2): The catalyst is first prepared on the substrate by electron-beam induced deposition in ETEM; a single nanotube could be grown directly onto this catalyst in an ETEM.

3.3.2 Potential High Impact Research Areas

Integrated processing and fabrication observed *in situ*

A very exciting goal is to perform all the processing steps *in situ* (deposition, oxidation, electrical contact formation), in particular on pre-patterned substrates that are compatible with

current manufacturing techniques. A combination of surface and bulk characterization techniques is clearly required here, as well as a high resolution imaging capability.
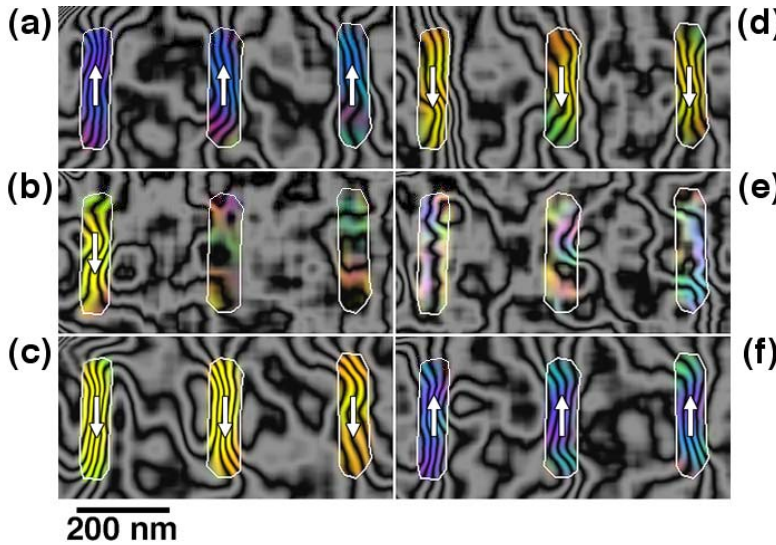
Figure 12a. Experimental magnetic induction maps, showing six different remanent magnetic states recorded using electron holography from three adjacent pseudo-spin-valve elements, examined in plan-view geometry. The outlines of the elements are shown in white. The contour spacing is 2π/64 = 0.098 radians, such that the magnetic flux enclosed between any two adjacent black contours is h/64e = 6.25 × 10⁻¹⁷ Wb. The direction of the magnetic induction in the elements is shown using arrows and according to a color wheel (red = right, yellow = down, green = left, blue = up) (Kasama et al., J. Appl. Phys. 98 (2005), 0139032005).
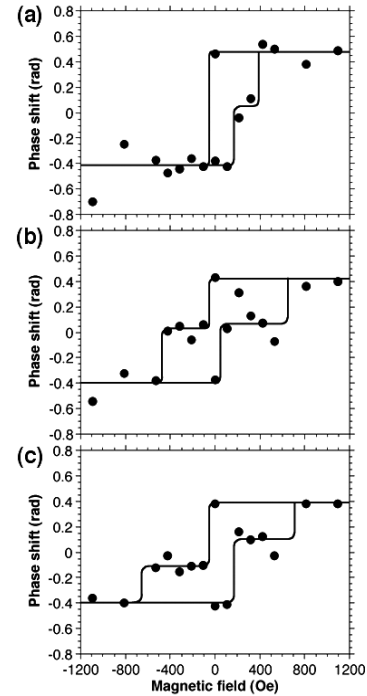
Figure 12b. Separate remanent hysteresis loops measured from each of the three elements shown in Fig. 12a, illustrating the variability in both the switching field and the projected induction in the elements. The loops in (a), (b) and (c) were obtained from the left, middle and right elements, respectively, shown in Fig. 12a.

Growth of nanowires

The possibility of growing composite prismatic structures, such as nanowires covered by dielectrics, appears particularly exciting since complete devices can be built in one nanostructure. An important objective is to understand quantitatively the growth of such materials, and the relationship between structure and growth conditions. Such insights would allow targeted synthesis of specific structures or devices, and combinations of structures.

Dynamic *in situ* TEM-STM experiments

Another challenge is to carry out the dynamic TEM-STM experiments in the precisely controlled environment (in terms of temperature and atmosphere) where electronic transport characteristics would be probed as a function of the environment to observe the *I-V* characteristics at various operating conditions, and thereby determine the environmental

conditions that best optimize the transport properties. To accomplish this would require modifications to the TEM column itself, as opposed to novel sample holder designs, where *in situ* processing, environmental control and other surface techniques could be added onto the TEM column for a truly unique hybrid processing-characterization instrument.

Nucleation and Evolution of Magnetic States

It is important to correlate magnetic fields in materials and devices that are of interest for storage, recording and biomedical applications with their structure, composition and defects, both during and after the controlled *in situ* application of magnetic fields, electrical currents and temperature. Problems of key interest include: the nucleation and evolution of magnetic states in thin films and nanoscale elements. Figures 12a, 12b and 13 are examples of recent electron holographic studies of magnetic systems. With such tools we can examine the following processes at the nanometer scale:

- Magnetic switching processes in random access and magnetoresistive elements;
- The motion of domain walls in the presence of an electrical current (the spin torque effect) and in nanowires in the presence of constrictions;
- Transitions between superparamagnetic, single domain and multi-domain behavior in magnetic thin films and nanoparticles;
- The effect of oxidation and temperature on nanocrystalline iron oxides of geological and biological interest;
- Details of the growth of magnetic thin films and nanostructures (*e.g.* ferromagnetic materials on antiferromagnets);
- The quantitative examination of vortex motion and pinning in low and high temperature superconductors.

For all of these experiments, it is important to be able to apply controlled magnetic fields of up to ~1 T during imaging. For some of them, it is also essential to apply electrical contacts to chosen regions of electron-transparent specimens.

The present state-of-the-art capabilities, developed by individual groups, should be commercialized to meet these challenges. Substantial improvements in the spatial resolution and sensitivity of magnetic imaging, with the ultimate aim of imaging single magnetic spins, mayrequire automation of the acquisition and analysis of hundreds or thousands of images of the same region of a specimen, with advanced specimen drift correction. For the examination of superconductors, the ability to routinely achieve a continuous range of specimen temperatures is essential, ideally to below about 10 K. For imaging domain wall motion and magnetization reversal processes in real time (on ps to ns timescale), pulsed electron, perhaps pump probe, experiments are ultimately required.

Ferroelectric materials

Ferroelectric materials are important materials displaying multifunctionalities and are widely used in capacitors, transducers, actuators, filters, sensors, and random access memories. All these functionalities rely on the cooperative ionic displacements and the alignment process of these displacements under electric fields. There are many issues still unsolved so far and *in situ* TEM can make significant impacts. These include the atomic mechanism of displacive phase transformation, electric field-induced ionic displacement alignment process (the polarization

switching), electric field-induced phase transition, and the size limit for the presence of ferroelectricity in nanostructures with low dimensions.

Direct imaging of the atomistic mechanism and kinetics of electric polarization switching under temperature, electric field, or mechanical stress would advance the current understanding of domain nucleation and growth mechanisms in these materials. Also, antiferroelectric oxides and relaxor ferroelectric oxides tend to transform to the ferroelectric state under strong electric fields below certain temperatures. In antiferroelectric compounds, antiparallel ionic displacements are expected, while in relaxor ferroelectric compounds, random and dynamically fluctuating ionic displacements are speculated. Strong electric fields are expected to align these ionic displacements and the alignment process corresponds to a first order phase transition. Direct imaging of the atomistic process of the electric field-induced phase transition will advance the understanding and determination of favorable conditions for such transitions.

Spintronic Materials

TEM has never been used to image ferroelectric domains in polymers and liquid crystals. *In situ* TEM techniques can be employed for direct imaging of polarization and switching of ferroelectric domains in these materials and is expected to make unique contributions due to its high spatial/temporal resolution.

While electronic materials exploit the transport of electrons across junctions, and magnetic materials exploit electron spin alignment in domains, recent developments in spintronic materials aim to combine the two functions by exploiting transport of spin polarized electrons. This development has the potential to merge the semiconductor based data processing functions
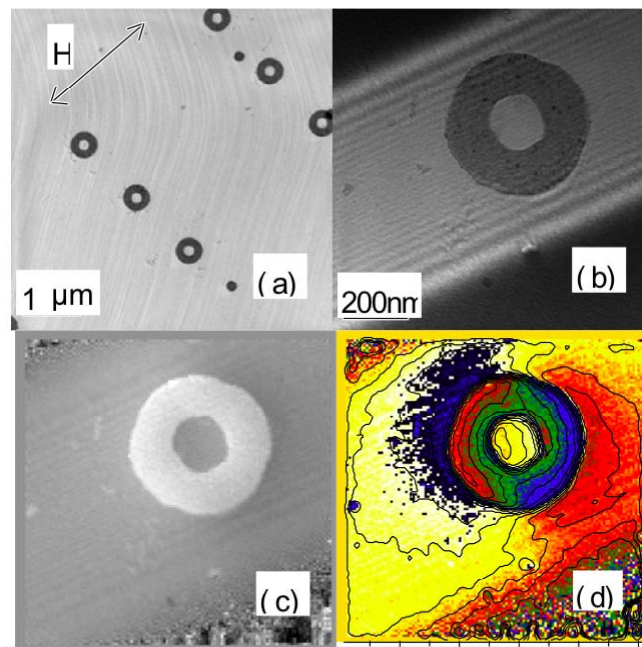
Figure 14. *(a) Series of Co rings with 400-nm outer diameter, 150-nm inner diameter. Applied field direction as shown. (b) Hologram of single Co ring from (a). (c) Reconstructed black and white phase image, which depends on in-plane magnetic induction. (d) (Color) Phase image in pseudo-contour-contrast mode. The real magnetic induction and stray field distribution are shown. Field lines are parallel to color lines. Contour spacing is 0.4 radians (Hu et al, J. Appl. Phys. 97 (2005) 054305).*

with the magnetic based data storage functions.

The search for spintronic materials has found its initial successes in the class of dilute magnetic semiconductors (Ohno, 1998). These are based on wide band gap semiconductors (like GaN, GaAs, ZnO…) with magnetic transition metal dopants (like Mn, Co…), with challenges coming from the need to push the Curie temperatures substantially higher than room temperature, and to overcome nanoscale phase separation in the films and at their surfaces and interfaces. Other approaches use magnetic tunneling junctions to provide spin polarized electrons, with challenges arising from the need to create ultra-thin insulating layers with ultra-smooth interfaces to the sandwiching magnetic layers. *Ex situ* microscopy has already been essential in the initial developments, but *in situ* microscopy has not as yet been applied to these novel material nanostructures. With the current instrumental capabilities it should be possible to study the transport of spin polarized electrons with high spatial resolution as a function of sample heating, biasing and magnetization by dynamical atomic resolution imaging and electron holography, diffraction and spectroscopy. *In situ* synthesis can have positive impact on new spintronic nanostructure developments.

Optical materials and devices

Devices and components taking advantage of the optical and opto-electronic properties of materials represent a key area of current and future research and development. For light-emitting systems, the *in situ* experiment requires stimulation of the photon production (*e.g.* by electrical biasing), exaggeration of the experimental conditions (*e.g.* voltage, temperature) to bring about more rapid changes, monitoring of the spectral response *from the area under examination* and then documenting the behavior by recording the sequential events in the electron microscope. Conversely for light-absorbing materials (*e.g.* photovoltaics), the influence of prolonged irradiation, both by polychromatic and monochromatic wavelengths, again under exaggerated conditions (*e.g.* intensity, temperature), concentrated on the field of view and monitoring the induced signal locally, would provide significant understanding of the performance, degradation and limitations of this class of materials. Furthermore, for beam sensitive materials such as organic LED's or photovoltaic polymers, the irradiation can be carried out without the electron beam, and specific areas can be recorded periodically under low dose conditions.

This type of *in situ* experimentation then requires the ability to either provide the stimulation locally (*e.g.* biasing) and/or to monitor it, combined with the ability to concentrate radiation and/or to measure emitted radiation, again on a local basis. This would probably involve both innovative design of the specimen holder and also the microscope environment to allow additional detectors and the introduction of the irradiation beam from the outside.

Phase change memories

Chalcogenide phase change materials are currently used for data storage, both in rewritable optical discs and "Ovonics" unified memory. Both of these make use of their readily induced transformation between crystalline and amorphous states and back again, accompanied by major changes in optical reflectivity and electrical conductivity. Despite this, many aspects of the phase transformations are poorly understood. Improving the understanding could lead to improvements in rewrite cycles, memory density, and possibly lead to new uses.

Challenges will be to image, at high speed, the phase change as it occurs in order to elucidate the phase change mechanism. In addition, advanced characterization techniques, such

as fluctuation electron microscopy have yet to be applied to these materials *in situ* to identify the dynamical aspects of medium range order.

Molecular Electronics

The aim of molecular electronics is to use individual molecules as building blocks for nanometer-scale electrical circuits. Recent scanning probe microscopy (SPM) studies have demonstrated that the atomic structure of the electrodes contacting the molecule and the nature of the molecule-electrode bond can have a dominant effect on the electrical properties of such a system (Hersam, et al., 2004). These studies include placing a molecule between two deposited nanowires serving as a source and drain, using an SPM tip as a gate to characterize the electronic properties of the device (Mativetsky, et al., 2003).

An extension of this work would be to probe the electrical properties of a molecular device while viewing its atomic structure in the TEM. Numerous studies have been done with an SPM in the TEM. Molecular devices could be placed on such a holder, probed by the SPM tip for any electrical changes, while monitoring the structural changes by TEM. Furthermore, using techniques to suspend single molecules between support electrodes in a TEM holder, the electronic structure of molecular electronics can be probed by electron energy loss spectroscopy (EELS). With further development of microscopes equipped with monochromatic electron sources, these EELS experiments can be performed at very fine energy resolution. Coupling this with aberration-corrected microscopes with sub-angstrom spatial resolution, minute changes in the electrical properties of molecular devices, possibly even local bonding changes between the individual atoms of a device, can be monitored.

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4   Nanoscale Processes in Structural Materials

4.1   Past Successes

One of the earliest triumphs of TEM in materials science was the confirmation that dislocations occur in crystalline materials (Hirsch *et al,* 1977). This feat required a deep understanding of the diffraction contrast mechanisms that are associated with strain fields in thin crystalline foils, and helped accelerate the growth of the new field of electron diffraction physics (Cowley, 1981). Early research succeeded in developing the methods for studying other types of defects such as stacking faults and precipitates.

It was quickly recognized that static images of defects do not reveal the underlying mechanisms associated with materials properties. The earliest *in situ* TEM studies of materials involved the design of sample stages that could apply stress and heat. The obstacles were related to the simple fact that TEM specimens must be located in the tight confines of the objective lens pole pieces and objective aperture, under high vacuum conditions in order to be compatible with the generation of a stable monochromatic electron beam. In the earliest TEM designs, construction of actuators, feedthroughs and heaters required watchmaker skills. Nevertheless, dislocation motion and crack propagation were observed at nanometer resolutions. Video recordings were made by directly recording from the phosphor view-screen. Interestingly, the earliest *in situ* reaction studies were of oxidative corrosion and its impact on mechanical properties (R. Milne and A. Howie, 1984, and references therein).

4.2   Current status

The deformation of solids depends on the generation and propagation of defects. In normal crystalline solids, these are generally dislocations, which are responsible for the plastic deformation. Understanding deformation processes remains critically important to numerous industries, such as aerospace and automotive manufacturing as well as in defense applications.

The development of stable side-entry specimen holders has allowed significant progress to be made in *in situ* studies of mechanical properties. The actuators and heaters can be designed into the holder, without any need for associated changes to the TEM column. Modern designs have overcome the issues related with vacuum integrity, and have largely solved the sample drift problems that occur as the holder settles against the vacuum seals, and the 'microphonic' coupling to the outside environment. In addition, precise tilting control and extended tilt range (for some sample geometries this can be almost a full 360° about one axis) has facilitated electron tomographic studies of heterogeneous materials.

Atomic resolution observations of defects can now be performed routinely. Both high-resolution bright-field images and annular dark-field images in the STEM, in combination with nanodiffraction, provide structural information in the neighborhood of defects and interfaces. Electron energy loss spectroscopy and x-ray dispersive spectroscopy now yield chemical information at the sub-nanometer level and under ideal conditions at atomic column resolutions. This combination of structural and chemical imaging at subnanometer levels is an important characterization tool for the present research thrust on nanostructural materials.
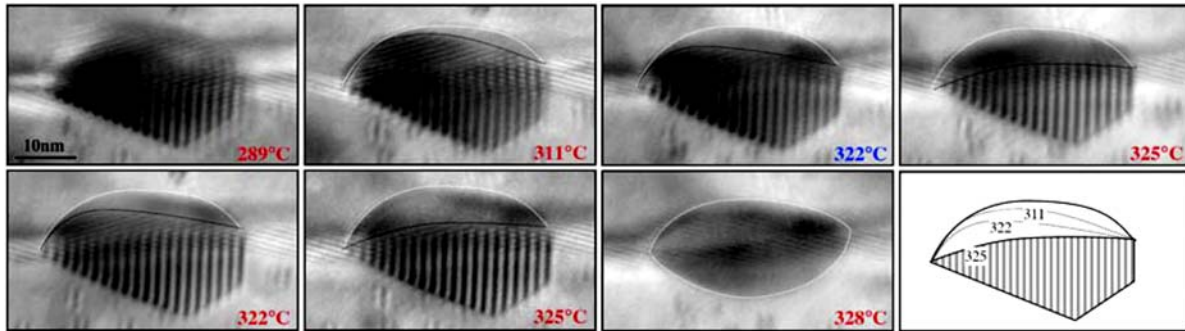
*Figure 14. Differential melting of Pb inclusion in an aluminum bicrystal. The interface structure depends strongly on the matrix orientation, hence one side is facetted whereas the other is rounded. On raising the temperature, the rounded surface melts first. Once the inclusion is fully melted, the inclusion shape changes and the matrix accommodates the change. Molten Pb inclusions in single crystal Al migrate by Brownian motion within the thin film (Dahmen et al., (1997) Phys. Rev. Lett. **78**, 471–474).*

The transition between the liquid and solid states is one of the most fundamental phase transformations. Despite its central importance in a great variety of processes and materials, its microscopic and dynamic aspects are not fully understood. In particular, the role of microscopic fluctuations and premelting in nucleating transitions are only now being investigated experimentally. Figure 14 shows an example of a study requiring a stable *in situ* heating stage with precise calibrated control of the temperature. In this study Pb inclusions in aluminum can be melted at temperatures near 325°C. However, the precise melting temperature depends in part on size and on the Pb/Al interfacial structure. In the example shown, the Pb inclusion is located at a grain boundary in the Al. At low temperature, part of the inclusion surface is rounded, and part is facetted where the interface structure can be made coherent without significant stress. By inspection of the diffraction contrast and Moiré fringes, it can be seen that pre-melting is initiated at the rounded interface near 322°C. However, it is not until 328°C is reached that the whole inclusion melts. In single crystal Al, where inclusions are not pinned at defects, the molten Pb migrates as a particle by Brownian motion, staying within the confines of the Al foil. By cycling through the melting transition, the mechanisms of stress relief can be imaged. Such mechanisms include dislocation loop punching, surface roughening and faceting.

An example of the effect of hydrogen on the shear stress experienced by an edge dislocation, due to the presence of another as a function of separation distance between the dislocations, is shown in Figure 15a. Also shown is the shear stress of the isolated hydrogen atmosphere. The decrease in the shear stress in the presence of hydrogen means that the separation distance between edge dislocations on the same slip plane will be less than in the absence of hydrogen. Figure 15b shows an array of dislocations piled up against a grain boundary in the absence of hydrogen. With the introduction of hydrogen into the sample, the dislocations in the pile-up move closer together and closer to the obstacle (Figure 15c). This shift

in position is more clearly seen in the comparison image presented as Figure 15d in which a negative image of the final position (white dislocations) is superimposed on a positive image of the initial position (black dislocations). Experiments such as these provided the initial impetus for developing the hydrogen enhanced localized plasticity model as well as verifying the predictions of the model.

In situ nano-indentation is an emerging technique that can reveal subtle details associated with plastic deformation at the nano-scale that is obscured by macroscopic indentation studies. Special TEM holders that use technology learned from the designs of atomic force microscopes allow a diamond tip, with radius of curvature less than 50 nm, to be positioned accurately near a
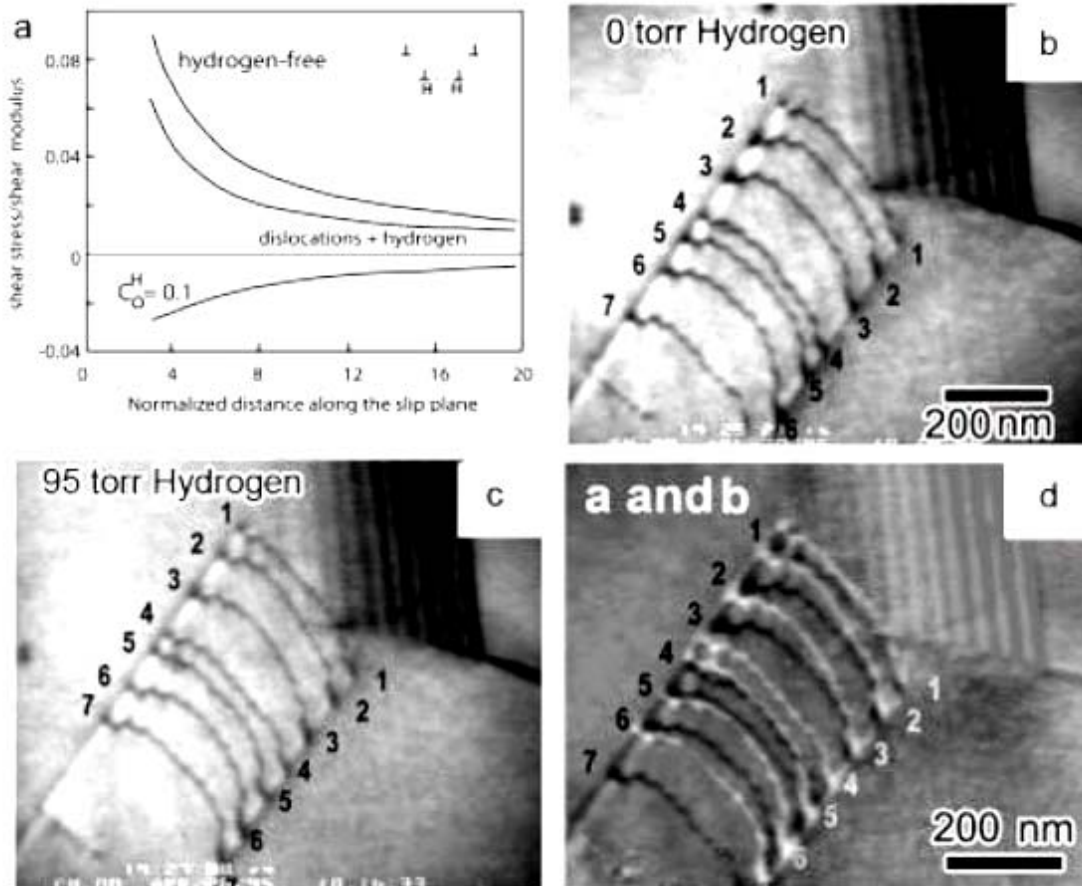
Figure 15. *Effect of hydrogen on shear stress experienced by one dislocation due to the presence of the other dislocation. Both dislocations are on the same slip plane (b-c) Reduction of separation distance between dislocation pile-up in 310s stainless steel in 95 Torr H_2. (d) Composite image made from a positive image of a (black dislocations) and a negative image of b (white dislocations). (d). (Ref. Birnbaum and P. Sofronis; (1993) Mater. Sci. Eng. **A176**, 191; I.M. Robertson; (2001) Engineering Fracture Mechanics **68**, 671).*

sample and then driven into a thin region of interest while observing in cross-section view (see Figure 16). Dislocation loops can be observed emerging from the stressed region. In addition, the role of grain boundaries near the surfaces, and the surface structure itself, are found to play an important role in the initial plastic deformation prior to dislocation migration. Surface oxide layers, although thin (~1nm), are also found to influence significantly the initial deformation behavior. Such results make it clear that bulk plasticity behaviors cannot be extrapolated to the

nanoscale where surface effects can dominate. The ability to image at the nanoscale while performing nanoindentation provides valuable information about the process.

Amorphous materials pose an interesting challenge to both imaging and diffraction characterization techniques. Unlike crystals, the averaging of scattering over regions of the sample interferes with the ability to resolve atomic positions. In TEM, the averaging effect is also known as the column approximation where the volume is governed by the sample thickness and the image point spread function (*i.e.* the resolution). Fluctuation electron microscopy, a hybrid imaging-diffraction statistics technique, has proven useful for detecting medium range order in disordered materials. This technique will be valuable for studying phase change memory alloys.
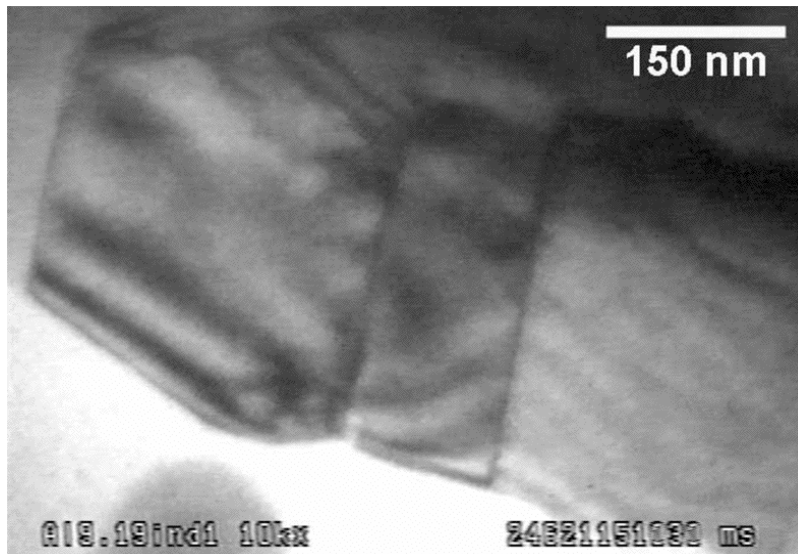
Figure 16. Bright-field TEM image showing the approach of a diamond nano-indenter (lower left) to the edge of a thinned Al film supported on a silicon wafer (upper right). Individual Al grains can be probed by the indenter while monitoring the stress and the strain. Such studies reveal plastic behaviors at the nanoscale that would otherwise be considered 'noise' in macroscopic indentation experiments. (Courtesy of E. A. Stach, A. Minor, Z. Shan, O. Warren, S. Asif, E. Cyrankowski and T Wyrobek).

Electron tomography is an emerging field that allows 3-dimensional reconstruction of heterogeneous materials at the nanometer scale. The principles are similar to x-ray holography. For electrons, the scattering signal needs to be monotonic with thickness, and relatively free of strong dynamical scattering effects. The annular dark field detector signal in the scanning transmission electron microscope provides such a signal.

It is noteworthy that the holography and tomography techniques rely heavily on accurate and sensitive image detectors that interface to computers (in these instances slow-scan CCD cameras), and require extensive algorithm development and computer processing. This trend towards more quantitative electron microscopy is driving many of the new developments in TEM as an analytical tool. In this vein, electron crystallography is an emerging area that allows the structure of complex nanocrystalline materials to be determined, when x-ray Rietveld or single crystal methods are ineffective at these small length scale. With few exceptions, most TEM detectors and techniques are applicable to *in situ* studies. The limitations appear to be mainly driven by the limited space around the objective lens area.

4.3 Future Challenges

The Structural Materials panel assembled the following list of future challenges. It is interesting that several of the topics are in traditional areas, such as dislocation studies. The reason that these fields are still vibrant is because TEM, as a technique, is still evolving. The improvements are not incremental. For example, the present development of aberration-corrected objective lenses opens up the possibility of revisiting older studies that were inconclusive because of inadequate microscope resolution at that time. In addition, the parallel development of image-detection hardware (particularly the fast image detectors) and image-processing software is also fueling this renewed interest.

4.3.1 Fundamental Questions and Current Challenges

Is it possible to image at the atomic level the 3-dimensional structures of dislocation cores during motion under applied stresses?

At present, such studies are hindered by the sample projection problem (possibly addressable by tomography), insufficient resolution (addressable by aberration-corrected lenses) and difficulties in calibrating the applied stresses. In addition, elastic relaxation effects due to the sample surfaces may make observations valid only for thin samples, and not for the bulk material.

Can the dynamical evolution of the Burgers vectors of 3-dimensional arrays of dislocations, moving under applied stresses, be characterized?

Although related to the previous question, these studies do not necessarily require high resolution. A 3-dimensional analysis of the time-evolving diffraction contrast images is required.

Can rapid phase transitions be observed?

Many physical processes occur at rates that are much faster than the acquisition speeds of present detectors (typically video rates of 30 frames per second). Image detectors capable of ~1000 images/second, or faster are desirable.

Can the structures of liquid-solid and vapor-solid interfaces be studied at high temporal and high spatial resolution?

Many solid materials grow by accretion of matter at surfaces from liquid or gas phases, or by direct deposition of particles. Diffusion of the arriving atomic and molecular building blocks can be rapid prior to reaching equilibrium at growth sites, and the surface structures may be in a dynamic equilibrium. Melting and solidification are related phenomena. The ability to acquire high-resolution structural data rapidly (with adequate signal-to-noise) is essential for studying the structural dynamics of such interfaces.

Can the structures of amorphous materials be studied dynamically near the glass transition?

At temperatures above the glass transition temperature T_g, amorphous materials begin to flow. However, at temperatures only just above T_g the glass remains essentially brittle, but IR studies show that a system of relaxation processes is activated. The nature of these relaxation mechanisms is still unknown. A challenging experiment would be to observe a thinned glassy

material near T_g *in situ* using fluctuation electron microscopy to study the fluctuations dynamically. High speed imaging systems would be desirable in order to observe the fast relaxation processes. Information learned might lead to a detailed understanding of diffusion, flow, and relaxation mechanisms in glasses.

4.3.2 Potential High Impact Areas

The following high impact research areas will benefit from advances made in the above-outlined challenges.

Dislocation studies

Substantial questions remain in this field, despite half a century of research. Critical challenges include:

- Imaging the dynamics of arrays of dislocations in response to applied stresses, with full characterization of all dislocation Burgers vectors in 3 dimensions. These studies are necessary to validate the substantial body of simulation work in the area of multi-scale modeling to predict mechanical behavior in materials.
- Imaging of dislocation cores at atomic level resolution during dislocation motion. The static structures of dislocation cores are just now being solved systematically with the latest aberration-corrected microscopes. While important, the understanding of static core structures yields only limited insight into core structures during propagation. Dislocation core structure evolution under applied stresses and heat is still relatively unexplored.
- Point defects are known to dramatically affect dislocation motion, and thus can strongly affect the yield response of materials. Understanding the role of point defects on dislocation motion via direct imaging is thus a critical challenge for the field.
- The specific structures and behaviors of 'metadislocations', found in quasicrystals, complex crystalline materials, and in metallic glasses, are still poorly understood.

Martensitic phase transformations

Again, there is still much that is unanswered in this mature field. Most studies have been made statically (see for example (Zhou, Aindow et al. 2004)). Martensitic phase transformations are of central importance to the shape memory alloy effect. They require no long-range diffusion to progress. They also have fixed orientation relations between the parent and daughter phase that contains an invariant plane strain condition. These transformations can proceed rapidly, which have made them historically difficult to observe *in situ*.

The growth kinetics of 'burst' martensites is controlled by the applied driving force, the interfacial structure and the development of growth stresses. The modeling of growth kinetics has been limited by the knowledge of the interfacial defect structure and how the motion of the defects mediates the advancement of the growing interface. *In situ* observation of the defect structure, for example misfit dislocations, with their motions would be useful for comparison to models. The main difficulty in making these observations is the speed at which the interface advances. A central challenge is therefore to:

- Develop high time resolution methods for studying rapid phase transformations. The interfaces can move at speeds of 10 – 1000 m/s. If we would like to limit the motion blur of the interface in the image to 10 nm, this would require exposure times of 1 ns to 10 ps. *In situ* diffraction patterns will also give information on structure and may reveal the strain pathway

that the transformation follows to change of the crystal structure.

- Develop event detection software in order to maximize the data collection efficiency. Given the high throughput of data with fast cameras it is crucial to only collect data once the event has been nucleated. This needs to be automated since human response times will be too slow.

Diffusion controlled transformations in thin films

Thin films are attractive not only because they reduce device dimensions but also because of their robust mechanical properties when compared to bulk materials. It is often the interfacial interaction or surface properties that enhance or degrade the functionality of thin films. The involved mechanisms that are well understood in bulk materials are driven differently in the environment of a thin film, and they must be better understood in order to create more reliable, stable devices. Diffusion controlled transformations that occur in thin films are often driven by various chemical potential gradients within or between the thin films, but the process and rate limiting mechanism of interface diffusion remains unclear.

Environmental stability is one of the most important properties for materials exposed to air or water. Much is known about oxygen interaction with metal surfaces and about the macroscopic growth of thermodynamically stable oxides. At present, however, the nanoscale 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 area.

To overcome these hurdles to studying thin film diffusion:

- Faster time-resolved imaging and diffraction at higher spatial resolutions than current *in situ* system capabilities are needed.
- Aberration-corrected TEMs fitted with precision tilting/heating stages, and with EELS and energy dispersive x-ray spectrometers are needed.
- Accurate control of environmental cell pressure and temperatures is needed.

Segregation and moving interfaces

Electron microscopy has made significant contributions to our understanding of the physical structure of stationary interfaces. Concepts and tools for analysis and prediction of interfacial properties have developed in parallel with the ability to test and verify their role in interface structure. A prominent example is the structural unit model of grain boundaries, which postulates that general grain boundaries are made up of characteristic structural units from a small number of delimiting boundaries that are nearby in configuration space. Such structural units have been identified by atomic resolution imaging in a multitude of boundaries in metals, ceramics and semiconductors, and their distortion or sequence in a particular interface has been observed directly and correlated with local properties. However, in contrast to the analysis of structure, the ability to detect and measure local composition, bonding or electronic structure on the sub-nanometer scale is just being developed. This development is made possible by the great recent advances in aberration-corrected electron optics, which permits finer electron probes with higher intensity and better spatial and spectral resolution.

Interfaces between liquids and solids are an important challenge since the details of nucleation and growth upon solidification are still largely unknown. Recent x-ray reflection studies on flat Bi-alloy liquid surfaces (Shpyrko, 2006) have shown some remarkable, and hitherto unsuspected structural properties. In particular, the discovery of liquid surfaces with periodic 2-dimensional ordering that persists for a few layers into the liquid. The buried layers

have strong composition dependence, persisting to ~3–5 layers and are crystalline within the plane of the crystal surface. Presumably, these surface-skin phases cannot exist isolated from the liquid-vacuum interface. Unlike solid crystals, the residence time of atoms at a particular site is likely to be short. Although the technological importance of such phases is not yet known, the study of ordering and of defect structures in these structures, and the relation to 'skin' properties, would constitute a new sub-field of materials study.

The challenges in this area are:

- To detect dynamic changes in atomic structure at solid-solid interfaces, and to identify the role of impurity atoms and of external stimuli such as temperature, stress and applied fields.
- To identify structural correlations at liquid-solid and liquid vacuum interfaces. This will require high-speed dynamic observations at high resolution. It would be very desirable to detect simultaneous changes in local composition.
- A related challenge would be to study the stability of liquid-liquid interfaces. Interesting phenomena should occur at the molecular scale when the liquids are immiscible. This too will require high-speed detectors.

Melting and solidification

This area is related to the previous topic. Melting is an ultrafast process in metals (Siwick, Dwyer et al. 2003). Questions still remain on how the structure is lost in the crystalline phase as it becomes liquid and how it depends on electronic structure and electronic temperature. An interesting example is how a metal melts when it is irradiated by an ultrafast (<1ps) laser pulse (H. Dömer and O. Bostanjoglo, 2003).

The photon energy is deposited into the electronic system of the metal and is transferred to the ionic system by electron phonon coupling that can take several ps to equilibrate. If the melting transition is fast compared to this timescale, then the melting is occurring in the presence of a large thermal depopulation of states. This change in electronic structure should change the interatomic interactions and may be manifested as an altered path towards the loss of structure.

Solidification is typically a much slower process. The solid phase must first be nucleated, which has a stochastic component. According to atomistic simulations, if more than one crystal structure exists with small energy difference, then these nuclei can compete and slow the solidification even more (Streitz *et al*, 2005). The *in situ* observation of crystal nucleus formation from the liquid would validate these theoretical predictions. It is desirable to be able detect dynamic changes in atomic structure at solid-solid interfaces, and to identify the role of impurity atoms and of external stimuli such as temperature, stress and applied fields.

High time resolution is needed to capture the dynamic events. In several cases a moving interface is required to be frozen in place by a "stop action" exposure. These exposure times will have to be less than 1 ns for interfacial velocities of 10 m/s or greater for 10 nm spatial resolution of the structure. This level of resolution is sufficient for features such as dislocations that can be imaged with conventional dynamical diffraction contrast mechanisms. To achieve this level of time resolution, pulsed operation of the electron beam is required (Dömer and Bostanjoglo 2003).

Radiation effects

Electron microscopy has been a major contributor in understanding radiation effects since the discovery of radiation-induced void swelling in the Dounreay, Scotland fast reactor (C. Cawthorne and E. J. Fulton, 1967). Research on the effect, which destroys the structural integrity of materials used in the cores of reactors designed to operate at high temperatures and high

neutron doses, showed that void formation is caused by radiation-induced vacancy supersaturation, leading to void precipitation. Alloy composition, nanostructure, and chemical segregation to nanostructural features such as grain boundaries, interfaces and dislocations have large effects on the magnitude and rate of void swelling. It is now known that appropriately chosen alloys/nanostructure can reduce void swelling, which will improve the economics of nuclear generated electricity. The theory for the effect is based on chemical rate theory for point defect aggregation in the presence of biased sinks, and is well developed to the approximately 100 Å spatial level.

Now there is new emphasis on nuclear power for electricity generation worldwide, particularly in the United States, resulting from carbon-based fuel concerns. New reactors will need to be designed that are safe and that minimize the risk of nuclear proliferation. These reactors will operate at high temperatures in high dose rate environments. For economic reasons, operation to the highest total doses possible with safety is desirable. New radiation-resistant materials for reactor construction could conceivably be developed from data obtained from *in situ* neutron radiation studies. Extending the useful life of power reactors and enhancing safety are obvious worthwhile goals and environmental microscopy can make major contributions here. The challenges for *in situ* TEM research in this area are to:

- Develop techniques that will allow the motion of individual point defects to be followed.
- Develop techniques to observe materials response to irradiation under reactor conditions.

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5 Other Areas of Potential Impact

Other areas of nanoscience were also discussed at the workshop. These areas were not covered in as much depth as the primary three focus areas, but we recommend them for further study. Brief summaries of the discussions are presented in this section.

5.1 Atmospheric Aerosols

A critical variable for understanding and predicting climate change is evaluating the radiative effects of the various constituents of Earth's atmosphere. According to the Intergovernmental Panel on Climate Change (IPCC 2001), major uncertainties exist in knowledge of the radiative forcing produced by aerosol particles, for which the "level of scientific understanding" is "very low." It is well known that clouds have a major effect on climate (through both "direct" and "indirect" effects), but quantifying those effects poses a major problem in global modeling and understanding climate change.
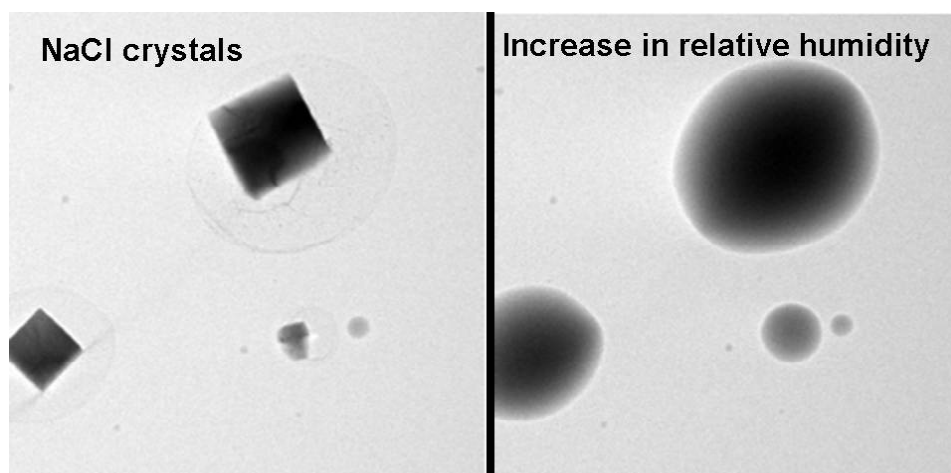
Figure 17: In situ deliquescence of nanocrystals of NaCl. Left shows a TEM image of particle in dry atmosphere and left show same particles in deliquesced state by raising vapor pressure in environmental cell of TEM (Courtesy M. Wise and P.Buseck).

70% of the Earth's surface is covered by water, and sea salts are major constituents of the atmosphere over and near the oceans. They are hygroscopic and can experience growth through deliquescence (the phase change whereby salts turn into liquid droplets through reaction with water; the reverse process of efflorescence, or crystallization, typically occurs at lower values of RH, called the ERH). Once deliquesced, the particles can become effective contributors to cloud formation. The relative humidity for deliquescence (DRH) for particles larger than ~100 micrometers is well known. There are, however, major uncertainties about the values for the DRH as particles become smaller and enter the nano-sized regime (Figure 17). To make advances in this area, we need:

- Methods to determine vapor concentrations gradients around efflorescing and deliquescing particles. Such quantification is much needed for comparing theory with experiment.
- Rapid image acquisition for following morphological and structural changes associated with

efflorescence and deliquescence.

In situ electron microscopy will be a powerful approach for answering some of these critical questions and further our ability to predict climate change.

5.2   Geological issues

The potential geological applications of *in situ* microscopy remain to be explored. Many rock-forming minerals experience oxidation/reduction or sulfidization reactions. Other minerals form through vapor-phase deposition, for examples as small crystals in vugs (cavities in volcanic and other rocks). These should, in principle, all be amenable to study using the ETEM. However, to date geological reactions have not been explored using *in situ* methods, but they remain an important research area for the future. The challenges in this area potentially lie beyond the current capabilities of *in situ* TEM. At present it does not seem possible to develop techniques that will allow high-pressure synthesis to be observed at high resolution in TEM. Observation of the nucleation and growth of minerals, such as zeolites, under hydrothermal conditions will provide us with the knowledge that could perhaps allow hypothetical zeolite frameworks, with predicted useful pore characteristics, to be efficiently synthesized. This would have enormous implications in the petrochemical and fine chemicals and relates directly to catalysis.

5.3   Biomineralization

The key question in all biomineralization is whether the organic molecule, often a protein, in some way controls the mineral crystallization and how the organic macromolecule is bonded to the mineral phase at the atomic level. In the case of the abalone shell, it has been shown that there are proteins that can change the mineral deposited from calcite to aragonite. The understanding of other systems is much less advanced and is usually based loosely on the hypothesis that de-protonated amino acid residues will electrostatically bind to surface calcium ions.

There is a pressing need for techniques to study the organic macromolecule/mineral interface at atomic resolution. This is an example of a solid-liquid interface that has not been accessible to TEM techniques, though in recent years imaging the growth of crystal facets in real time using liquid cell AFM has yielded interesting new information about the surfaces. *In situ* TEM would provide answers to important questions on what mineral surfaces are like in the presence of ionic solutions. For proteins it is still controversial whether they retain their 3D conformation in proximity to a mineral surface, or whether they totally or partially denature.

A combination of an *in situ* liquid cell TEM and tomography could give significant insights into the biomineralization process, which would have broad implications for the treatment of bone-related diseases (osteoporosis) and diseases involving pathological biomineralization such as urolithiasis.

5.4   Biological materials

In situ electron microscopy on biological materials was first investigated in the 1980's by several groups, including the examination of crystalline arrays of biomolecules by Butler and Hale (1981), the contraction of muscle myofibrils by Fukushima et al. (1986) and the work from the laboratory of Parsons, who introduced the concept of a separate chamber in the microscope column sealed off from the high vacuum by electron-transparent material. The initial ideas of observing living organisms under an electron beam still have applications, such as studying the

mechanisms of microbial metal reduction for bioremediation as well as biofilm formation. The dynamics of ATP-induced shortening of muscle myofibrils could only be visualized at the resolution of the electron microscope (Sugi et al., 1997), and experiments with assemblies of actin associated with various actin-binding proteins, whose actions exhibit lifetimes of several seconds, are perfect candidates for *in situ* studies. In this category we can also directly observe other cytoskeletal elements, such as microtubule arrays, as they appear for instance in mitosis, or in general polymerization and depolymerization cycles.
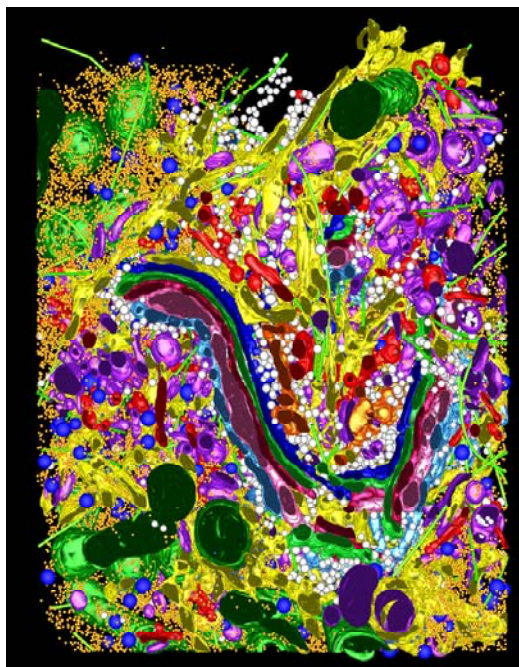
Figure 18. *An electron tomographic reconstruction of the Golgi apparatus, into which have been modeled the endoplasmatic reticulum, membrane-bound ribosomes, microtubules, mitochondria (Marsh et al., 2001).*

        In situ microscopy probes the relationship between biomolecular structure, reactivity and selectivity that are the basis for molecular engineering of novel nanostructures. Inspiration for additional applications using *in situ* EM can come from confocal microscopy, where in essence living cells are visualized with selective markers. The ultimate extension of *in situ* microscopy for these studies would be to perform electron tomography (Figure 18) experiments in real time – that is, probe the complete 3-dimensional structure of these components as they transform.

References
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Marsh, B.J., Mastronarde, D.N., Buttle, K.F., Howell, K.E. and McIntosh, J.R., (2001) "Organellar relationships in the Golgi region of the pancreatic beta cell line, HIT-T15, visualized by high resolution electron tomography", *Proc. Natl Acad. Sci.* vol. **90**, , 2399-2406.
Sugi, H. et al. (1997) *PNAS* 94:4378-4382.

6 Novel Tools and Facilities

One task for workshop participants was to reevaluate our current capabilities in order to meet the current and future scientific challenges. It was universally agreed that *in situ* observations need to be complemented by theoretical modeling. In addition, current instrumentation needs to be further improved and new techniques need to be developed. Special instruments and theoretical calculations will be expensive to acquire and to maintain; therefore new funding models need to be developed. Detailed outcomes for these three components are described below.

6.1 Theoretical Modeling as an Adjunct to *In Situ* Microscopy

In situ microscopy is invaluable for following chemical reactions at the atomic scale but the detailed knowledge of the reaction paths is presently limited by the resolution of the electron microscope. Theory can play an important role in identifying a reaction path and its energetics. A reaction can be modeled in a supercell that contains a few surface layers and an adsorbate. Atom positions can be relaxed to achieve a minimum energy configuration, and the energy of the system tracked along a postulated reaction coordinate as the reaction proceeds. The energy barriers along different paths can be calculated and the most probable path selected. Alternatively molecular dynamics techniques can be used to seek a reaction path when there are no clear a-priori choices for the reaction coordinate.

The biggest limitation in modeling, based on first principles quantum theory relevant to *in situ* microscopy, is the size of the system. At present it is possible to study simple molecules on unreconstructed surfaces with fewer than 100 atoms. To describe realistically large adsorbates with up to 30 atoms, or to explore what might happen on reconstructed surfaces, much larger supercells with up to 500-1000 atoms are needed. There are two barriers for performing such calculations. Computation time scales as N^x where N is the number of band electrons and x is some power between 2 and 3 depending on the method. For this reason a number of theoretical groups are working on order N methods where scaling is linear rather than quadratic or worse.

Another problem is that as the system gets larger, with more degrees of freedom, the global minimum becomes harder to find, and a whole set of local minima might have energies close to the global minimum (the ultimate example of this is protein conformations!). Here quantum based molecular dynamics such as those introduced by Car and Parinello (1985) might be appropriate.

6.2 Instrument Development for Dynamic Experiments in TEM

Many instrumental developments and improvements were identified that could dramatically improve the impact of *in situ* TEM. All these improvements could be incorporated in a single instrument, a dream instrument for dynamic characterization making a "Molecular Observatory". Some of the developments are described below.

6.2.1 Sample Preparation and Drift Correction

Specimen preparation for TEM observations is an age-old, and a difficult issue. Remarkable progress has been made, particularly with focused ion beam (FIB) instrumentation, but some of the future challenges require further developments. For example, most ferroelectric

oxides are ferroelastic and very brittle making specimens extraordinarily fragile. Improved nano-manipulation methods are needed, particularly for applying electrodes.

Another problem for dynamic measurements is image drift during heating and cooling, or while the sample is under the influence of electrical or magnetic field. Again, some groups have developed linear drift correctors, but universal availability of such systems is imperative to obtain atomic level structural and chemical information from dynamic processes.

6.2.2 Improved structural and spectral resolution

Most of the future applications of *in situ* techniques require (a) detection of adsorbates on the surface of nanoparticles, (b) direct imaging of vacancies and their motion, (c) atomic level imaging and spectroscopy of the dislocation cores, (d) direct imaging of ionic displacements of 0.01 Å (particularly for ferroelectrics), (e) site-specific electrical and magnetic measurements at nanometer scales, and (f) direct imaging of electron spin ordering with sub-nanometer resolution. Many of these requirements can be accommodated by aberration-corrected microscopes with large objective lens pole-piece gaps, which provide room for much of the additional instrumentation. Such microscopes are currently being developed and will probably be available within the next five years. There are still some challenges, for example, measuring electron spin ordering in spintronics materials that still require further developments.

6.2.3 Improved Environmental TEM

Currently available ETEMs are restricted to 10-50 Torr of gas pressure and maximum temperatures of 1000°C. These are still far from the reactor conditions in which industrial catalysts operate. Therefore an ETEM with a tolerance for higher temperature and pressure conditions, while maintaining subatomic resolution capability, will allow us to make observations near reactor conditions. Moreover, such instruments are also needed to observe the movement of defects, grain boundaries and dislocations in electronic, optical, magnetic and structural materials under the influence of corrosive environments.

In order to obtain thermodynamic and kinetic data from these experiments, measurements must be quantitative. So an accurate measurement of local sample temperature and the local pressure, gas flow and composition during reaction is essential.

6.2.4 Incorporating Other Characterization Techniques into the TEM Platform

The results that have been obtained so far have highlighted specific areas of instrument development that would significantly enhance our understanding of catalyst function. In addition to observation of the morphology of supported metal clusters, the development of imaging schemes to simultaneously observe the surface structure would complement the analysis. This could be achieved through an integrated SPM inside the TEM, or possibly through robust diffraction reconstruction methods. At the present time, EELS can be used to observe adsorbates of 1-2 monolayers on the surfaces of nanoparticles. The sensitivity of the method needs to be improved to allow individual molecules to be detected. With improvements in energy resolution to analyze both the vibrational spectrum and electronic structure of these adsorbates, a direct picture of the active sites on the nanoparticle surfaces will be obtained. Other spectroscopic probes, such as Raman, IR and even possibly EXAFS, in conjunction with TEM would provide additional insights. Finally, we note that present ETEM capabilities allow study of the catalyst materials, but not the gaseous reactants and the products, *i.e.* the catalysis process itself. The

ability to analyze the products of catalytic reactions, localized to individual sites, is highly desirable. This may be achieved through ultrafast electron diffraction, localized mass spectrometry or a nano-sniffer device. Although such needs are perhaps beyond the capabilities of present-day technology, their future development as a by-product of the emerging nanotechnology boom is not implausible. Finally, the data obtained from *in situ* observations needs to be coupled with computational approaches to aid in the interpretation of reaction mechanisms.

6.2.5 Novel TEM Holders

Continued advances in TEM holders, such as wet-cell TEM and electrical cell holders, will allow researchers to determine structural and electrical properties of hydrated, or even live specimens. Coupled with advances in instrument resolution with aberration correction, one can envision studying the process of a synapse firing. It could be possible to induce a nerve cell to fire, while studying any structural or electrical property changes in the electron microscope.

6.2.6 Fast Detectors for Dynamic Imaging

Though many of the results presented at this meeting were in terms of "before" and "after" images, video recording of experiments in progress is a critical component of the dynamic microscopy toolset. (Video, more generally defined as a continuous stream of images in time, and not necessarily NTSC will be called "dynamic imaging"). Some experiments rely explicitly on temporally calibrated dynamic imaging. Two examples are the measurement of reaction rates in carbon nanotube formation and the measurement of stochastic parameters of diffusing particles. Other experiments that don't explicitly require motion analysis still need the insight gained through live viewing of the experiment in progress and also the ability to review and analyze the experiment later. In all cases, more resolution and speed would be desirable. Many important applications, such as crack nucleation and phase changes, however, have experimental evolution time scales that are orders of magnitude faster than the frame rates of conventional cameras.

The ability to perform dynamic time-resolved microscopy is intrinsically limited by the number of electrons in the beam. Three types of experiments are possible. Most microscopists think in terms of a continuous stream of image data in TEM mode with a constant current incident on the specimen. Typical beam currents are between 1 nA and 10 nA with recording at video rate of 30 frames per second. This means that there are between 6×10^9 and 6×10^{10} electrons per video frame. Assuming images have the NTSC resolution of 440×480 pixels there are an average of 750 electrons per pixel. Assuming one wants to detect a minimum of 8 contrast levels, 64 electrons per pixel would be necessary on a perfect detector. Typical camera DQEs are between 0.07 and 0.7 across the spatial frequency- and kV- range of interest, thus requiring between 100 and 1000 electrons per pixel. This means that at the resolution and sensitivity of current cameras, we are already at (or close to) the practical limit of frame rate. Increases in either the frame rate or in the resolution in terms of number of pixels per frame will require improvements in detector sensitivity (DQE) and possibly also new designs for the illumination systems of microscopes to maximize beam current. The table below shows the approximate beam current needed to properly dose cameras of various pixel resolutions and frame rates assuming a perfect (DQE=1) detector.

Format	horizontal	vertical	bit depth	fps	MB/s	I(700 e/pix) (nA)
NTSC	440	480	8	30	6.0	1.4
Gatan SC1000 binned x4	1002	668	14	15	16.8	4
NTSC at 100fps	440	480	8	100	20.1	5
HDTV	1920	1080	16	30	118.7	28
4K Digital Cinema	4096	2048	12	24	288.0	68
"Machine Vision"	1280	1024	8	1000	1250.0	294
1Mfps burst camera	1024	1024	10	1E+06	1 250 000.0	293 601

To study phenomena on shorter time scales one has to adopt a completely different approach. For example phase transformations would require following events with 10 ps to 1 ns time resolution. The only practical way to achieve this is to trigger the event with an ultra-short laser pulse and then form the image from an electron burst triggered by a second laser with an appropriate time delay (see for example work of Geoffrey Campbell). At present, electron pulse lengths are limited to 1.5 ns with 10^7 electrons due to source brightness and coherence requirements in the presence of the Boersch effect. Reducing the number and/or increasing the size of pre-specimen crossovers should allow 10^8 or more electrons per pulse which would yield 380 electrons per pixel in a 512×512 image. Going to high (5MeV – Stanford) voltage will further reduce the Boersch effect but will require special cameras to maintain high DQE with a high-voltage electron beam. For phenomena that can be repetitively cycled such as some ferroelectric transitions, a further technique would be to cyclically excite the specimen and beam source and accumulate signal-to-noise. A third approach, which would be useful for following phenomena on the microsecond time scale, would be to combine a high-speed machine-vision burst camera with a series of laser-generated pulses whose duration matches the total image burst recording time of the camera, which, in the example in the table above would be 100 µs for 100 images. Laser-stimulated-emission sources can in principal meet the ~300 µA (average) beam-current needs of this method, but source heating may be an issue.

Data format is another important issue. Videotape makes acquisition of large amounts of video data easy but makes subsequent review, analysis and reduction difficult because it is non-quantitative, does not easily permit attachment of parametric data and is serially accessed. Digital dynamic imagers generating image streams with parametric metadata would not only facilitate analysis and reduction of experimental data but also, by facilitating more efficient experiments through feedback and control, would reduce the absolute quantity of data that would be needed to be recorded. Since the community is used to using non-quantitative videotape until now, a digital format with both non-quantitative high compression for compactness but also with mathematically loss-less compression for numerical processing would have great value. Motion JPEG2000 is an example of one such format and has been recommended for use in medical imaging, an application very analogous to dynamic microscopy in its requirements for dose-efficiency, spatio-temporal resolution, data integrity and scalable transportability.

6.3   Facilities and Funding Models

6.3.1   Regional Facilities

Dynamic TEM experiments require specialized instrumentation that is either developed in house or custom built by a manufacturer. The experimental needs vary depending on the nature of the dynamic event being studied and the instrument or specimen holders may require

constant modification and development. For researchers interested in investigating a number of these processes for a given material system, it is impractical (not to mention prohibitively expensive) to own all the instrumentation necessary to carry out these experiments. Similarly, researchers at smaller institutions who need to make a few experiments to confirm their *ex situ* observations may not be able to afford one of these microscopes and the expertise required to maintain them.

A solution to these issues is to establish and develop centralized regional facilities. Similar ideas have recently been present in a report by the National Research Council entitled "Midsize Facilities: The Infrastructure for Materials Research" and can be found at the following link: http://www.nap.edu/catalog/11336.html. This study found that the escalating cost of specialized tools for materials research at the nano-scale level makes it impossible to place instruments at every research location, or even at a majority of them. The study recommended the adoption of a number of strategies for the funding agencies, the host institutions, and for the research community itself, largely involving the establishment of a number of regional shared facilities, well distributed throughout the United States. Our workshop participants echoed the same general feeling. The overall structure for such facilities should be:

- Centralized instrumentation for all aspects of *in situ* TEM applications.
- Centralized expertise to maintain, develop and assist users from other institutions.
- Remote access.
- Should have federal funding for maintenance, development and replacement costs for instrumentation hosted in such facilities.
- Should have federal funding to support remote teaching.
- Should have federal funding to support visiting experts who are interested in future developments that can be used by general scientific community.

Such regional facilities will provide a platform to expand the capabilities of groups of researchers. They will not only reduce the cost of duplicating instrumentation but will also provide centralized pools of expertise to assist users in experimental design and implementation. The advent of remote microscopy makes these centralized facilities accessible to an even broader range of users. Remote microscopy has been demonstrated for a variety of instruments. All modern microscopes are fully digitally controlled, and all functionality of the instrument can be accessed through a control computer. Through client-server software, the control computer can be accessed and controlled via the Internet with a remote control station. With the spread of high-speed Internet connections, and the advent of Internet2 for research purposes, remote control of a microscope becomes comparable with local control. Commands from the remote station access the instrument in real time while data from the instrument returns to the remote for immediate feedback. This allows a researcher to access advanced *in situ* instrument at a remote site and perform dynamic experiments simply by purchasing a standard PC and remote control software.

An additional benefit to remote microscopy is education and training. Currently, researchers must travel to a specific facility to learn how to perform a dynamic experiment. Through remote microscopy, real time movies of dynamic events can be transmitted directly to classes in schools, community colleges and university. Graduate student training classes can be held from the facility with the instrument to simultaneously educate and train a number of potential users. Regional facilities for *in situ* TEM could also drive new developments in response to requests by users. Such facilities could develop and test novel combinations of *in situ* techniques and make this evolving instrumentation available to the scientific community. Many

of the novel instrument development discussed in Section 6.2 of this report would be ideal projects for these regional facilities. The facilities could hold remote open houses and workshops to bring users up to speed on the latest developments and their potential applications.

6.3.2 Funding Model

Federal agencies could fund regional facilities by supporting instrument acquisition, development and infrastructure to optimize access and efficient use. The development costs of unique instruments (aberration-correctors, plus an enhanced arsenal of special detectors) could be more than $5M per instrument. The service contracts would be an estimated 4–5% of the cost of the instrument ($250K or greater). Two types of staff, technical and PhD research levels would be necessary. The technical staff is needed for maintenance and development of the instrument, whereas research staff will be a conduit to the scientific community, and will provide training and education of students and post-docs. Improvements in remote and digital microscopy are necessary to optimize use and reduce overall costs (*e.g.* travel) as well as permit remote teaching of courses.

References
Car R and Parrinello M (1985) Phys Rev Lett 55 , 2471

7   Education, Outreach and Workforce Needs

Nanoscience will play a vital role in almost all aspects of future technology, and it is important that we develop a workforce that can fully recognize and exploit the new opportunities that are presented by this exciting field. Strong education and outreach programs will play a central role in ensuring that the workforce of the future is fully aware of the fundamental concepts behind nanoscience. Nanoscale imaging techniques have a unique role to play in these education programs because they provide the windows that allow us to see directly the nanoworld. *In situ* techniques allow us to see the nanoworld in action and provide compelling visualizations that demonstrate fundamental scientific concepts. Combining reaction models with video images is an effective way to explain dynamic processes occurring at the nanoscale. The movies and animations generated directly from *in situ* observation should be extensively integrated into education and outreach programs.

Education programs should be developed for all education levels and different target audiences. These programs should include K-12, undergraduate and graduate education, community college students and school teachers. Specific activities that could enhance, develop and support educational activities in schools include:

- Develop nanoscience summer courses for high school teachers (teacher enhancement) to make K-12 students aware of the current technologies.
- Develop educational modules and websites based on dynamic *in situ* TEM observations (including videos) for nanoscience and technology curricula.
- Invite school children onto campus for tours to experience cutting edge research in nanotechnology.
- Encourage school science competitions in the area of nanoscience and nanotechnology.

At universities, research groups should be encouraged to integrate research results into curricula by developing undergraduate and graduate degree courses on nanoscience and technology. Currently, a handful of universities in the USA have undergraduate and graduate degree programs in nanoscience and nanotechnology. Such curricula can be established as;

 (a) an integrated course taught by interdisciplinary teams,
 (b) courses organized around applications,
 (c) appropriate laboratory modules,
 (d) courses based on academia-industry liaison.

Apart from regular traditional formats for education (formal undergraduate and graduate level courses for nanoscience and technology), there is a need for additional novel avenues to help engage undergraduate students in science and the nanoworld. Web-based libraries and courses can be the first steps in this direction. For example, in Pennsylvania, the different universities with Materials Science and Engineering departments (Univ. Pittsburgh, Carnegie Mellon University, Lehigh University, Penn State, Univ. of Pennsylvania) are developing a suite of graduate level courses that can be viewed remotely. This program will serve as a test-site for remote teaching of advanced electron microscopy, including *in situ*. NSF does provide specific funding for undergraduate education through their Nanoscience Undergraduate Education (NUE) program. But this program needs to be expanded to further broaden its impact
(see http://www.actionbioscience.org/education/uddin_chowdhury.html).

Other activities that can expand and broaden the educational and societal impact of *in situ* nanocharacterization include:

- Organize special schools/workshops to teach *in situ* TEM techniques and their applications.
- Present research accomplishments at non-microscopy related conferences, symposia and other meetings.
- Increase interaction between nanoscience research groups and local science museums and the media to facilitate public education on nanotechnology.

8 WORKSHOP PROGRAM

Dynamic *in situ* electron microscopy
as a tool to meet the challenges of the nanoworld

January 3-6, 2006 Tempe, Arizona

Organizers
Renu Sharma (Chair), Peter Crozier and Mike Treacy
Arizona State University

Tuesday, January 3, 2006 Katchina Ballroom Sections 1-3

7:30	Registration/Breakfast/Tentative Small Group Assignments
8.45	Welcome – Renu Sharma
9.00	Welcome - Glenn Schrader, National Science Foundation

Mostly Liquid Related

9.15   *Real time observations of liquid phase growth processes*
F. M. Ross
IBM T. J. Watson Research Center, Yorktown Heights, New York, USA

9.40   *Shape equilibration, melting and motion of Pb inclusions in Al*
U. Dahmen, T. Radetic, L.H. Zhang and E. Johnson*
National Center for Electron Microscopy, LBNL, Berkeley, USA and
* Ørsted Laboratory, Niels Bohr Institute, University of Copenhagen, Denmark

10.05   *In situ melting of nanoembedded metals and alloys: Problems and prospects*
K.Chattopadhyay
Department of Metallurgy, Indian Institute of Science, Bangalore, India 560 012

10.30   **Break - Katchina Ballroom**

Mostly Strain/Deformation

10:50   *Advances in understanding of fundamental phenomena in low dimensional semiconductor structures by in situ TEM*
Robert Hull
University of Virginia, Charlottesville USA

11:15   *FIB and TEM for in situ analysis*
Robert Sinclair
Department of Materials Science and Engineering, Stanford University, Stanford, California 94305-2205, USA

12:05   *Quantitative in situ nanoindentation in the TEM*
Eric A. Stach,[1] A.M. Minor,[2] Z. Shan,2 S.A. Syed Asif,[3] E. Cyrankowski,[3] T.J. Wyrobek,[3] and O.L. Warren[3][1]
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12:30	**Lunch - Top of the Rock Katchina Ballroom Sections 1-3**
1:40	Description of Group Process
1:55	Short Presentations of Future Needs/Burning Issues/Outstanding Problems and Identification of 3 – 4 Topic Areas
3:30	Formation of Small Working Groups, Appointment of Group Leader, Directions to Small Group Rooms

3:40 **Break – Poolside Small Group Rooms**

4.00   First Brainstorming Session of Working Groups

Katchina Ballroom Sections 1-3
5:30   Wrap-up Session
6.00   Finish

Wednesday, January 4, 2006 Katchina Ballroom Sections 1-3

7:30   **Breakfast**

Catalysts - In Memory of Leroy Eyring

8:30   *In situ TEM for studies of morphological changes in emission control catalysts during operation*
C. Wang[1]; J.H. Kwak[1]; D.H. Kim[1]; J. Szanyi[1]; R. Sharma[2]; S. Thevuthasan[1]; C.H.F. Peden[1]
[1] Institute for Interfacial Catalysis and Environmental Molecular Sciences
[2]Laboratory, Pacific Northwest National Laboratory, Richland, WA, USA. [2] Center for Solid State Science, Arizona State University, Tempe, AZ, USA.

8:55   *Dynamics and mobility of nanoparticles in heterogeneous catalysts*
Abhaya K. Datye[1], Lani Miyoshi Sanders[1], Ron Goeke[1], Thomas Hansen[1,2], Stig Helveg[2], Poul Hansen[2],Bjerne Clausen[2],
[1]Ceramic and Composite Materials Center, University of New Mexico, Albuquerque, NM 87131, USA, [2]Haldor Topse A/S, Nymollevej 55, DK-2800 Lyngby, Denmark

9:20   *Understanding the nature of heterogeneous catalysis and catalysts: Challenges and opportunities*
Jingyue Liu
Monsanto Company, 800 N. Lindbergh Blvd., St. Louis, Missouri 63167, USA

9:45   *In situ TEM observation of photo-catalytic TiO_2 films prepared by pulse-laser deposition method*
N. Tanaka, K. Yoshida and T. Nanbara
Ecotopia Science Institute and Department of Crystalline Materials Science Nagoya University, Chikusa-ku, Nagoya, 464-8603, Japan

10:10   *Atomic-scale imaging of metal nanocluster catalysts in their working state*
Stig Helveg
Haldor Topsøe A/S, Nymøllevej 55, DK-2800 Kgs. Lyngby, Denmark

10.35   Break- Katchina Ballroom

In situ Tools – In Memory of John Wheatley
10:55   *Image detector performance requirements for in situ electron microscopy*
             Paul Mooney
             Gatan, Inc.
11:20   *Notes on the nano-revolution: Revealing the nano-scale*
             Tom Isabell
             JEOL USA, Inc. 11 Dearborn Road, Peabody, MA 01969
11:45   *What are the most pressing needs for new dynamic experiments?*
             Jan Ringnalda, Mike Stekelenburg, Emile Asselbergs, Jan Meulensteen, Matthijs de
             Moor, Ronald Marx and Andre Sprankenis
             FEI Company
12:10   *Dynamical in situ microscopy: Using theory to fill in the gaps*
             Peter Rez,
             Department of Physics and Astronomy, Arizona State University, Tempe, AZ 85287

12:35 **Lunch – Top of the Rock Katchina Ballroom Sections 1–3**

1:45   Group Presentations and Discussion/Feedback/Adjustment

             Small Group Rooms
2: 45   Small Group Work – Reconsideration, prioritize for next 10 years, discuss how to
             achieve priorities, plan and delegate writing

4:00 **Break – Poolside Katchina Ballroom Sections 1-3**

4.20   Group Presentations and Discussion/Feedback/Adjustment

6.00   **Finish**

06:30   **Cash Bar**

07:00   **Conference Banquet – Garden Café**

Thursday, January 5, 2006 Katchina Ballroom Sections 1-3

7:30   **Breakfast**

Dynamic Properties Katchina Ballroom Sections 1-3
08:30   *A versatile three-contact electrical biasing transmission electron*
             microscope specimen holder for electron holography and electron
             tomography of working devices
             Rafal Dunin-Borkowski,
             Department of Materials Science, University of Cambridge, Pembroke Street,
             Cambridge CB2 3QZ, UK
08:55   *In situ TEM study of the electric field-induced phenomena in ferroelectric*
             ceramics
             Xiaoli Tan,

Department of Materials Science and Engineering, Iowa State University, Ames, Iowa, 50011

09:45 *Applying the dynamic transmission electron microscope to study the a to b phase transformation in Ti*
Geoffrey H. Campbell, Thomas B. Lagrange, Wayne E. King, Nigel D. Browning, Michael R. Armstrong, Bryan W. Reed, Judith S. Kim, Alan M. Frank, Brent C. Stuart, William J. DeHope, Benjamin J. Pyke, Richard M. Shuttlesworth, Frederic V. Hartemann, and David J. Gibson
University of California, Lawrence Livermore National Lab, Livermore, CA 94550

10:10 *In situ microscopy of small particles at ambient temperatures*
Matthew Wise and Peter R. Buseck
Department of Geology, Arizona State University, Tempe AZ 85287

10:35 **Break - Katchina Ballroom**

10:55 *In situ and position selective CVD of nanostructures with electron microscopy*
Kazuo Furuya, Guoqiang Xie, Minghui Song and Kazutaka Mitsuishi
National Institute for Materials Science (NIMS), 3-13 Sakura, Tsukuba 305-0003, JAPAN

11:20 *The surface kinetics of the initial stages of copper and copper alloy oxidation*
Judith C. Yang
Materials Science and Engineering Department, University of Pittsburgh, Pittsburgh, PA 15261, USA

11:45 *Atomic scale characterization of vacancy segregation and ordering in oxide*
N. D. BrowninG[1,2], C. J. Mitterbauer[1] and R. F. Klie3,[1]
[1]Department of Chemical Engineering and Materials Science, University of California, Davis, CA 95616, USA
[2]Materials Science and Technology Division, Chemistry and Materials Science Directorate, Lawrence Livermore National Laboratory, Livermore, CA 94550, USA, [3]Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, NY 11973, USA

12:10 *Polar oxide surfaces and interfaces*
Marija Gajdardziska-Josifovska
Department of Physics and Laboratory for Surface Studies, University of Wisconsin Milwaukee

12:35 **Lunch – Top of the Rock**

1:45 Discussion and Coordination of Writing

Small Group Rooms
2:00 Small Group Work – Write Draft of Report Sections
3:00 **Break – Poolside**

3: 20 Small Group Work – Write Draft of Report Sections

Katchina Ballroom Sections 1-3
5:30 Wrap-up Session

6:00   Finish

Friday, January 6, 2006 Katchina Ballroom Sections 1-3

7:30   **Breakfast**

8:30   Progress Reports/Discussion on Report Writing

Small Group Rooms
9:00   Small Group Work – Finish Report Sections

10:30   **Break - Katchina Ballroom Small Group Rooms**

Katchina Ballroom 1-3
10:50   Small Group Work – Finish Report Section
11:30   Wrap-up

12:00   **Lunch – Top of the Rock**

1 List of Participants

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2 Focus Groups

Focus Group 1: Catalysts and Nanomaterials for Energy, Environmental and Chemical Applications

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