SYMPOSIUM MM

In-Situ Electron Microscopy of Materials

November 28 - 30, 2005

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* Invited paper

SESSION MM1: Mechanical Properties I
Chair: Paulo Ferreira
Monday Morning, November 28, 2005
Hampton (Sheraton)

8:30 AM *MM1.1
Mechanical Behavior and Deformation Mechanisms of Nano Grained Thin Metal Films. Khalid Hattar[2], Jong Han[1], Ian Robertson[2], Taher Saif[1], Sean Hearne[3] and David Follstaedt[3]; [1]Mechanical and Industrial Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois; [2]Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois; [3]Sandia National Laboratory, Albuquerque, New Mexico.

Nano grained metals differ from their large grained counterparts in two distinct ways: they have abundant grain boundaries, and their grains may be too small for dislocation dynamics to be favorable. Hence, their deformation characteristics are likely to be dominated by grain boundary mechanisms, which are yet to be fully clarified. In this talk, we will briefly review the current state of understanding on the mechanical behavior of nano grained metals, describe our approach of studying free standing nano crystalline samples in-situ in SEM and TEM, summarize our experimental findings, and draw conclusions on possible grain boundary mechanisms. We have developed a novel micro mechanical stage that allows uniaxial testing of nano grained samples as thin as 30nm. The stage and the sample are co-fabricated using micro lithography and etching techniques. The combined setup can be used in SEM and TEM for in-situ inspection of the sample and its micro structure while its stress-strain response is measured. The method is applied to study sputter deposited aluminum films. We find, as grain size decreases below 50nm and sample thickness is 100nm or less, Al shows (a) non-linear elasticity, (b) reduced elastic modulus, (c) reduced strain hardening, and (d) reduced strain gradient strengthening. In-situ TEM observation shows little dislocation activity even under large stresses in grains 100nm or less. However, as thickness increases to 500nm (with average grain size 100nm), Al shows dislocation activity and large plastic deformation. In-situ TEM and SEM observations further reveal that thinner samples fail in a brittle manner by fracture with cracks (orthogonal to the loading direction) advancing primarily through grain boundaries, and by generation and coalescence of small cracks ahead of the primary crack. Mechanistic explanations will be discussed to interpret the experimental findings.

9:00 AM MM1.2
Local Deformation Behavior and Damage Evolution in MMCs Resolved by In-situ SEM Experiments. Otmar Kolednik, Klaus Unterweger, Miloslav Ognianov and Ronald Schoengrundner; Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Leoben, Austria.

An experimental study is performed to investigate the role of the composite architecture on the plastic deformation, crack initiation, and crack growth of particle reinforced metal matrix composites (MMCs) under monotonic loading. In-situ tensile and fracture mechanics tests are performed in the scanning electron microscope (SEM). Images are captured at different stages of deformation, and pairs of these images are processed by a digital image analysis program in order to identify physically identical (homologue) points on the specimen surface. The homologue points form a displacement field which is derived numerically to generate maps of the local in-plane strains and the rotation. The analysis yields displacement profiles along arbitrary lines and the local strain fields at the different loading stages with very high accuracy and lateral resolution (up to 600.000 homologue points per image). The investigated material is a powder-metallurgically processed, particle reinforced MMC with an Al6061 alloy as matrix material and SiC particles. The particle size, the particle volume fraction, and the aging conditions are varied. For comparison, the un-reinforced matrix material is also tested. In this way, the initial stages of plastic deformation, the formation and evolution of the shear band pattern, and the increasing damage by particle fracture and particle/matrix decohesion in the tensile specimens is investigated in great detail as a function of the composite architecture. The damage evolution in the tensile specimens is compared to those within the crack tip fields of the fracture mechanics specimens. The experiments are attended by mean-field calculations to estimate, for individual particles, the maximum normal stresses at the point of particle fracture and decohesion.

9:15 AM MM1.3
Length Scale Effect on Deformation and Failure Mechanisms of Ultra-Fine and Nanograined Metals. Khalid Hattar[1], Jong H. Han[2], David Follstaedt[3], Sean J. Hearne[3], Taher A. Saif[2] and Ian M. Robertson[1]; [1]Material Science and Engineering, University of Illinois, Urbana, Illinois; [2]Mechanical and Industrial Engineering, University of Illinois Urbana-Champaign, Urbana, Illinois; [3]Sandia National Laboratory, Albuquerque, New Mexico.

The deformation and failure processes in ultra-fine and nanograined metals over different length scales have been probed using transmission electron microscopy (TEM), scanning electron microscopy (SEM), and x-ray diffraction techniques in combination with a micromechanical in-situ straining device. The novel straining device provides a direct correlation between the mechanical properties and the controlling mechanisms by providing stress and strain data during observation of the deformation processes. This combination has revealed that increased film thickness results in a transition between limited plasticity and intergranular fracture to global plasticity and shear failure for sputter deposited aluminum samples of similar grain size. Other factors influencing the mechanical properties and governing mechanisms of deformation will also be discussed. This talk will compare and contrast the microstructural response of various material systems to the current understanding of the field.

9:30 AM *MM1.4
Nanoscale Probing of Stress Fields Using the Local Velocity of Misfit Dislocations in Heteroepitaxial Systems. Robert Hull[1], Chi Chin Wu[1] and Eric Stach[2]; [1]Materials Science and Engineering, University of Virginia, Charlottesville, Virginia; [2]Materials Engineering, Purdue University, West Lafayette, Indiana.

The velocity of propagating misfit dislocations in lattice-mismatched heteroepitaxial systems is controlled by the stress in the system. By varying the epitaxial layer thickness, composition, and geometry in the GeSi/Si system, we have made detailed correlations of velocity-stress in these structures, using direct in-situ observations in the transmission electron microscope (TEM). Over many years of experimentation, we have constructed universal stress-velocity curves comprised of several hundred independent measurements. While such measurements are important in understanding and predicting the strain relaxation kinetics in these systems, we can also use the instantaneous dislocation velocities as a measurement of the local stress environment. This enables measurement with sensitivity of tens of MPa, and spatial resolution of tens of nm, or better. We have used this approach to study fundamental phenomena in several configurations using in-situ TEM: (1) Dislocation-dislocation interaction stresses, by examining events where dislocations with orthogonal line directions intersect (2) Pinning stresses between propagating dislocations and impurity environments, created by ion implantation into the epitaxial layers. (3) Periodic stress field variations arising from surface topography created as a parallel strain relaxation mechanism.

SESSION MM2: Mechanical Properties II
Chair: Ian Robertson
Monday Morning, November 28, 2005
Hampton (Sheraton)

10:30 AM *MM2.1
In-Situ TEM Study of Confined Deformation Processes. Marc Legros, CEMES-CNRS, Toulouse, France.

Preparing a thin foil out of a bulk material before observing it through transmission electron microscopy (TEM) has long appeared as a source of artifacts or at least as an undersampling process. Correspondingly, thin foil effects have often been put forward to question the relationship between micro- or nano-scale dislocations mechanisms observed during in-situ straining experiments and conventional mechanical tests. Because many modern materials are engineered as thin films or nanostructures, this technique now appears remarkably relevant. In-situ straining TEM is one of the only technique allowing the dynamical observation of dislocation nucleation, multiplication and interaction processes. If one now considers that the significant volume, or grain size is on the order of several tens of nanometers, it means that most of the deformation processes happening in this small volume could be captured. We will focus here on the input of this technique on the understanding of the mechanical behaviour of small-scale systems such as metallic films (Al, Cu) bonded to a rigid substrate or free standing nanostructured Al metallic films. In both cases, in-situ straining TEM has revealed that anticipated mechanisms such as dislocation glide and cross-slip coexist with less expected mechanisms such as interfacial dislocation dragging and ultra fast GB motion. These observations provide key elements to gauge existing models of plasticity in confined crystalline matter and uncover possible new ones.

11:00 AM MM2.2
In-situ TEM observations of dislocation motion in passivated ultrathin copper films. Guillaume Wiederhirn[1], Thomas J. Balk[2], Gerhard Dehm[3], Julie Nucci[1], Gunther Richter[1] and Eduard Arzt[1]; [1]Department Arzt, Max Planck Institute for Metals Research, Stuttgart, Germany; [2]Department of Chemical and Materials

Engineering, University of Kentucky, Lexington, Kentucky; [3]Erich-Schmid-Institut fuer Materialwissenschaft und Department Materialphysik, University of Leoben, Leoben, Austria.

A solid understanding of thin film plasticity is essential to ensure the reliability and lifetime of thin film devices. We studied the influence of microstructural size effects and interfaces on dislocation behavior in 25 nm to 2 μm thick copper films ultrahigh vacuum sputtered onto amorphous-SixNy coated (111) silicon substrates. The copper films were coated with 10 nm of aluminum, which was oxidized to form an aluminum oxide passivation layer on the surface. Thermomechanical behavior of the films was investigated by the wafer curvature method. Dislocation plasticity was studied with in-situ transmission electron microscopy by cycling the samples thermally between room temperature and 500°C. The main focus was placed on the interaction of the dislocations with the substrate/film and film/passivation layer interfaces. The stress at 50°C exhibits two regimes; it is inversely proportional to the film thickness for films between 2 μm and 200 nm and exhibits a stress plateau at 1.3 GPa for films thinner than 100 nm. The behavior between 2 μm and 200 nm can be explained by either a combination of a Nix-type dimensional constraint and a Hall-Petch-like grain strengthening mechanism or by constrained dislocation source activation, as predicted by the model of von Blanckenhagen. In-situ transmission electron microscopy revealed dislocations in both twin and grain boundaries. Unexpected sessile parallel glide dislocations were also found in the thinner passivated samples and could explain the strength plateau.

11:15 AM MM2.3
In-Situ TEM Mechanical Resonance Studies of Carbon Nanopeapods Grown on FIB-Patterned Substrates.
Papot Jaroenapibal[1], Yeonwoong Jung[1], David Luzzi[1] and Stephane Evoy[2]; [1]Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania; [2]Department of Electrical and Computer Engineering, University of Alberta, Edmonton, Alberta, Canada.

The recent development of hybrid carbon nanotube materials, such as supramolecular self-assembled arrays of C_{60} molecules encapsulated within single-wall carbon nanotubes (C_{60}@SWNT), has opened new possibilities for the development of nanomechanical devices of tunable properties. We have studied the mechanical properties of empty and C_{60}-filled single-walled carbon nanotube bundles through observations of their mechanical resonances in a transmission electron microscope (TEM). Our custom designed specimen holder allows us to directly observe the mechanical resonance of nanotubes under external AC actuation. An average ratio of $(E^*/\rho)^{1/2} = 19002 \pm 2307$ m/s was extracted from the resonance analysis of the C60-filled bundles, compared to a ratio of $(E^*/\rho)^{1/2} = 13230 \pm 3187$ for the unfilled material. These values correspond to an effective average Young's modulus of $E^* = 240 \pm 105$ GPa for empty bundles, and of up to $E^* = 650 \pm 156$ GPa for the C60-filled materials. The significant increase of stiffness after filling observed here is believed to be dominantly related to an increasing of the strain energy of the system upon the deformation of C_{60} chains. In order to observe the filling effects on mechanical properties of each individual tube, we have created setups for characterization of isolated individual unfilled and C_{60}-filled SWNTs. We have used patterned features created with Focus Ion Beam (FIB) milling in Mo substrate to guide the growth of single walled carbon nanotubes. This FIB-patterned substrate helps increased control over directionality of chemical vapor deposition-grown SWNTs. The patterned substrate also serves as a map for which individual nanotubes can be followed through a series of filling processing steps, and the same nanostructure can be inspected by high-resolution TEM and therefore be stiffly clamped by a conducting nanoscale electrode formed by FIB metal deposition. Preliminary results have shown that isolated SWNTs with diameter 1.5- 2 nm and length up to 5 um can be successfully synthesized. We will present the in-situ TEM mechanical resonance studies of these recently fabricated nanostructures.

11:30 AM *MM2.4
Nanomechanical Size Effects on the Deformation Behavior of Silicon.
Daibin Ge[2], Andrew M. Minor[2], Oden Warren[4], Syed Asif[4], J. William Morris[3] and Eric A. Stach[1]; [1]School of Materials Engineering, Purdue University, West Lafayette, Indiana; [2]National Center for Electron Microscopy, Lawrence Berkeley National Laboratory, Berkeley, California; [3]Department of Materials Science & Engineering, University of California, Berkeley, California; [4]Hysitron Incorporated, Minneapolis, Minnesota.

Nanoindentation is widely accepted as the preferred technique to study localized mechanical deformation phenomena in materials. However, the mechanisms of deformation can only be inferred from the load-displacement data obtained during a typical instrumented nanoindentation test. In order to elucidate the underlying physics of these processes, we have developed the technique of in-situ nanoindentation in a transmission electron microscope. In this technique, a sharp diamond is positioned in plane with the edge of an electron transparent sample. The tip is then driven into the material in order to induce deformation and the corresponding response is observed in real time and at high spatial resolution. In this presentation, I will focus on our recent studies of the indentation response of single crystal silicon. Numerous studies of instrumented indentation into bulk silicon have shown that deformation proceeds via a complex pathway involving a combination of plastic deformation and phase transformations induced by the combined action of high hydrostatic pressures and shear loading. The exact pathway is known to depend strongly on the loading rate and the details of the tip shape. Using a combination of quantitative in-situ and ex-situ experimentation, we have shown that as the size of the volume under test decreases, the deformation pathway changes dramatically and the resulting load-displacement characteristics vary greatly from those observed in the bulk. In particular, once the characteristic length of the indented volume decreases below about 1.5 micron, the samples are no longer sufficiently large to support the high pressures necessary for the usual phase transformations to occur. Ex-situ instrumented measurements of the load-displacement clearly reveal a size-dependent softening of the material under these conditions, and in-situ TEM observations allow direct attribution of this to an increased tendency for dislocation nucleation and propagation in these samples. Additionally, upon release of the load the samples may undergo amporphization, with this being more likely to occur when the indenter is held in the material for extended periods of time during at it's maximum penetration. Throughout the presentation, emphasis will be placed on the need to correlate in-situ qualitative observations with quantitative measurements in order to fully explain the observed phenomena.

SESSION MM3: Mechanical Properties III
Chair: Gerhard Dehm
Monday Afternoon, November 28, 2005
Hampton (Sheraton)

1:30 PM *MM3.1
In Situ Studies of Nanoindentation in Metal Films.
John William Morris[1], Miao Jin[1] and Andrew Minor[2]; [1]Materials Science, Univ. of California, Berkeley, California; [2]National Center for Electron Microscopy, Lawrence Berkeley National Laboratory, Berkeley, California.

In-situ nanoindentation within a transmission electron microscope has been used to study the deformation mechanisms that govern the behavior of ultrafine and nano-grained materials. Five distinct mechanisms of dislocation-grain boundary interactions have been observed. In materials with relatively clean and mobile boundaries, such as pure aluminum, boundaries migrate in response to the imposed load, and coarsen through the spontaneous aggregation of adjacent grains. In alloyed materials with less mobile boundaries, such as Al-Mg alloys and martensitic steels, strain is transmitted across boundaries by dislocation migration or absorption-and-emission processes without significant local displacement of the boundaries. Finally, in at least one example, strain is accommodated by spontaneous recrystallization into a nanograined structure. These mechanisms all provide means for controlling hardening and promoting plastic ductility. Their possible use in the design of ultrafine-grained alloys with useful ductility will be discussed.

2:00 PM MM3.2
Using CBED to Locally Measure Strains in Al Lines during Thermal Cycling and Electromigration.
Julie Ann Nucci[1], Stephan Kraemer[3,1], Eduard Arzt[1] and Cynthia A. Volkert[2,1]; [1]Arzt, MPI for Metals Research, Stuttgart, Germany; [2]Forschungszentrum Karlsruhe, Karlsruhe, Germany; [3]Dept. of Materials Science and Engineering, University of California at Santa Barbara, Santa Barbara, California.

In situ local measurement of sub-threshold strains generated during the electromigration of a 0.3 micron wide Al interconnect was performed for the first time using convergent beam electron diffraction (CBED) in a TEM. Thermal strains were also analyzed and provided verification for the electromigration analysis. Spatially averaged strains resulting from thermal cycling and electromigration quantitatively agree with models and data from previous studies. However, the local strains exhibited variations as large as 2x10-3. After eliminating other possible mechanisms, the strain inhomogeneity is attributed to local plasticity through source-limited dislocation activity.

2:15 PM MM3.3
In-situ TEM Study of Thermally Induced Voids in 180 nm Cu Interconnects.
Jin Ho An and P. J. Ferreira; University of Texas at

Austin, Austin, Texas.

As Cu interconnects continue to decrease in width (to the current 100 nm dimension), microstructural features change dramatically. First, grain structures evolve from equiaxed type grains for large interconnect widths to predominately bamboo structured Cu lines for nano/submicron widths. Second, strain accommodation due to thermal stresses generated during thermal cycling shifts from a dislocation nucleation and motion mechanism operating in large interconnect widths, to void formation exhibited by nano/submicron Cu interconnects. As the formation of voids emerge as a crucial reliability issue for Cu nano-interconnects, particularly at high temperatures and high current densities, this study addresses the void formation behavior in damascene 180 nm Cu interconnects with predominately bamboo microstructures. For this purpose, the texture and grain morphology of these Cu interconnects is first identified herein. Subsequently, in-situ transmission electron microscopy (TEM) heating experiments are performed, so that void formation can be observed in real time. This enables the identification of preferential sites for void formation. Typically, voids form at triple junctions, specifically at the interface between two grains and the Cu/diffusion barrier (DB). A relationship between void formation and crystal orientation is established, in order to identify preferential stress-assisted diffusion paths, which control void migration.

SESSION MM4: Magnetic/Electrical Properties
Chair: Hiro Saka
Monday Afternoon, November 28, 2005
Hampton (Sheraton)

3:30 PM *MM4.1
In-situ TEM studies of magnetisation reversal processes in magnetic nanostructures. Amanda Petford-Long, Materials, University of Oxford, Oxford, United Kingdom.

The rapid increase in information storage density and also in memory density and speed have been brought about in part by the development of new materials, often consisting of layered structures, with properties that are engineered by controlling the microstructure and chemical profile of the layers. The layer thicknesses are of the order of a few nanometres, and the deposition techniques used mean that the films tend to be polycrystalline, resulting in variations in properties across the structures. One of the most spectacular examples is the development of devices based on the giant magnetoresistance (GMR) phenomenon, such as the spin-valve and the spin-dependent tunnelling junction used for read heads or magnetoresistive random access memories. In addition, patterned single layer structures are of importance for both media and memory applications. The behaviour of these materials relies on the local magnetic domain structure and magnetisation reversal mechanism, and one of the techniques enabling micromagnetic studies at the sub-micron scale is Lorentz transmission electron microscopy (LTEM) which allows the magnetic domain structure and magnetisation reversal mechanism of a FM material to be investigated dynamically in real-time with a resolution of a few nm. We have used LTEM and in-situ magnetising experiments to make qualitative and quantitative studies of magnetisation reversal in a range of materials including spin-tunnel junctions, patterned thin film elements and magnetic antidot arrays. Quantitative analysis of the Lorentz TEM data has been carried out using the transport of intensity equation (TIE) approach. Studies of active spin valves (i.e. ones through which a current is passed) have shown the way in which the magnetisation reversal process depends on applied current. In addition to the local variations in the magnetic properties induced by the microstructure of the films, further variations arise when the films are patterned to form small elements and results will be presented for a range of structures patterned both from single layers and from device structures.

4:00 PM MM4.2
In-situ TEM observation of electromagnetic field in some real materials. Katsuhiro Sasaki[1], Masatoshi Nakanishi[2], Kotaro Kuroda[1] and Hiroyasu Saka[1]; [1]Nagoya University, Nagoya, Japan; [2]Fuji Photo Film Co. Ltd., Minamiashigara, Japan.

Electromagnetic fields in some real materials have been observed by using electron holography and a novel method named Shadow Image Distortion (SID) method which we are developing. Mean electrostatic potential distribution across a p-n junction in a compound semiconductor has been observed during applying reverse bias using both methods. The sensitivity of both methods was compared. Magnetic field distribution surrounding a nano-sized magnetic particle has been observed by electron holography. Magnetic and structural phase transformation at an elevated temperature were investigated by in-situ TEM observation.

4:15 PM MM4.3
In-situ direct measurement of electrical properties of micron size Metal-Oxide-Silicon (MOS) capacitor by using Nanoprobe embedded Scanning Electron Microscopy (SEM). T. Zheng, Y. Ai, D. K. Cha, J Huang, G. Pant, H. Jia, M. J. Kim, R. M. Wallace and Bruce Gnade; Electrical Engineering, University of Texas at Dallas, Richardson, Texas.

As microelectronic devices continue to scale, electrical characterization of individual device structures become more important. In the past, the electrical properties of devices are measured using a conventional probe station. However, due to the intrinsic limitations of the optical system, as well as the positioning accuracy of the probe, it is impossible to directly and accurately probe submicron size devices with conventional systems. To overcome such limitations, measurement can be transferred to an SEM-based probing platform. By using the F-100 Nanoprobe system from Zyvex Inc., we have for the first time successfully measured electrical properties of MOS capacitors in a field emission SEM, and developed a protocol for in-situ electrical measurement inside a dual column FIB/SEM. For 100μm MOS capacitors, the results obtained from the SEM based platform are consistent with results from a state-of -the art optical-microscope based platform (Cascade Summit Probe Station). During the measurement process, the damage to the dielectric layer caused by exposure to electron beam irradiation has been carefully evaluated and minimized. The measurement environment is carefully controlled and optimized to reduce the background noise and maintain the standard deviation of the noise to $\sim$ 100 aF. This technique makes it possible to directly explore electrical properties of various sub-micron size electrical devices, especially their C-V behavior. Potential applications of the technique include probing molecular memory structures, metal gate materials with different micro structures, and materials for high precision analog circuits.

4:30 PM *MM4.4
Quantitative Magnetic Imaging and In-Situ Magnetization of Patterned Magnetic Elements. Yimei Zhu, V. V. Volkov and J. W. Lau; Brookhaven National Laboratory, Upton, New York.

Understanding magnetic structure and magneto dynamics of magnetic building blocks is crucial to the development of modern magnetic storage media and spintronic devices. With the ever decreasing size of magnetic elements, the ability to quantitatively characterize individual magnetic objects at nanoscale under various environment becomes particularly important. To achieve these goals we acquired a custom-made field-emission TEM equipped with a long-focal-length objective lens (the only one of its kind in the US), specializing in high-resolution magnetic imaging and holography. We developed and fabricated special in-situ stages with a Hall-probe to calibrate local magnetic field and Helmholtz coils to apply in-plane magnetic field to the sample. To quantitatively measure local magnetization at different length scale we also developed and implemented microscopy techniques including off-axis electron holography and a phase retrieval method based on the electro-optical transport-of-intensity approach [1]. In this presentation, we will first review these capabilities. We then show the magnetic domain evolution of patterned arrays of Permalloy and Co squares and their magnetic structural transition as a function of the applied magnetic field and field-switching or reversal rate as well as temperature. By quantitative analysis of the local magnetization based on in-situ experiments, we explain why a parent state (S-state) will result in two different low-energy ground states (vortex state and seven-domain state) and how the energy barrier to the magnetic vortex nucleation can be derived [2]. We will also present our in-situ magnetization experiments on disk arrays that are composed of a tri-layer (magnetic-nonmagnetic-magnetic) structure. Due to the coupling between the two magnetic layers (magnetized parallel or anti-parallel), the system can have two distinct stable states and is ideal for the applications of magnetoresistive random access memory (MRAM). New results using a magnetic force microscope built into a TEM stage to locally induce magnetic field and field gradient and to change magnetic polarization of individual elements to study element-element interaction and magnetic reversal behavior will be also reported. Collaborations with M. Beleggia, M. Schofield, J.K. Bording, K. Buchanan and S. Bader are acknowledged. This work was supported by Division of Materials Sciences, Office of Basic Energy Science, U.S. DOE, under contract No. DE-AC02-98CH10886. [1]. V.V. Volkov and Y. Zhu, Phys. Rev. Letters, 91, (2003) 043904. [2]. J.W. Lau, M. Beleggia, M. Schofield, G.F. Neumark, and Y. Zhu, J. Appl. Phys. 97 (2005) 10E702.

SESSION MM5: Phase Transformations
Chair: David Follstaedt
Tuesday Morning, November 29, 2005
Hampton (Sheraton)

8:15 AM *MM5.1
In-situ observations of phase transformations in titanium.
R. C. Pond[1], G. Seward[2], J. Wheeler[2] and D. Prior[2]; [1]Engineering, University of Liverpool, Liverpool, United Kingdom; [2]Earth and Ocean Sciences, University of Liverpool, Liverpool, United Kingdom.

We have used the CamScan X500, a scanning electron microscope optimised for high-temperature experiments, to observe the HCP to BCC phase transformation in commercially pure titanium, at temperatures above 882 degrees C. The BCC phase nucleates as both intracrystalline plates and grain-boundary allotriomorphs. Electron backscatter diffraction analysis shows that intracrystalline plates have a Burgers orientation with the parent HCP grain ({0001} // {110} and <11-20>//<111>). Boundary plane orientations and topography associated with plates suggest that their growth involves a shear mechanism. Grain-boundary allotriomorphs exhibit the Burgers orientation with one of their neighbouring HCP grains. The boundary plane orientations are arbitrary and have no associated topography, suggesting that allotriomorphs grow by a diffusive process. Direct observations of boundary motion and textural analysis show that, during HCP to BCC transformation, the BCC phase microstructure and texture are dominated by the growth of grain boundary allotriomorphs, rather than intracrystalline plates. The transformation from BCC to HCP has also been observed, again with the formation of allotriomorphs and intragranular plates. However, the dominant feature of the resulting microstructures depended on the cooling rate.

8:45 AM MM5.2
In-situ Observations of Martensitic Transformation in Ti.
Thomas Bradley LaGrange, Geoffrey H. Campbell and Wayne E. King; Materials Science and Technology Division, Lawrence Livermore National Laboratory, Livermore, California.

Martensitic transformations occur by a rapid lattice-distortive mechanism, where kinetics and morphology of the transformation are dominated by the strain energy. Since no diffusion is involved in these transformations, phase fronts move near the speed of sound. From technological viewpoint, these transformations are integral processes in engineering of structural materials, and understanding such processes is necessary for tailoring the microstructural and mechanical properties. Although martensitic transformations have been extensively studied for over a century (especially in Fe-based alloys), many questions remain regarding the nucleation mechanisms and growth kinetics. This is partly due to the fact that the transient events occur too rapidly, even at cryogenic temperatures, to be captured by conventionally experimental techniques. The current models of the martensite nucleation and growth have either been based on post mortem observations or inferred from results using idealized cases feasible for laboratory study. Due to the lack of concrete experimental data, these models cannot comprehensively explain all modes of martensite growth, especially burst martensite. Recent advents in ultrafast electron microscopy at Lawrence Livermore National Laboratory have led to the development of a dynamical transmission electron microscope (DTEM) that combines all of the powerful techniques of the standard TEM with nanosecond time resolution and is suitable for capturing dynamic processes, such as martensitic transformations. Using this instrument, the transient microstructural states of β phase (bcc austenite) to α (hcp martensite) transformation in pure Ti were studied. To induce the transformation, the TEM foil was heated with a 20 nanosecond laser pulse above the Ms (1100 K). The microstructural changes and transformation dynamics were imaged using 2 nanosecond (at FWHM) electron pulses in phase with the sample drive laser. The dislocation dynamics of the glissile interface between martensite and parent phase were studied as well as the influence of the local microstructure, i.e. grain boundaries and other martensite variant interfaces, on the dynamics of the transformation. The structure and mode of propagation of these variant interfaces is a crucial factor in the resultant variant morphologies and size. These observations will be discussed in frame of a theoretical transformation dislocation models that have appeared in the literature. This work performed under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

9:00 AM MM5.3
Observation of a Hybrid Displacive-Diffusional Ordering Phase Transformation Mode in Near Equiatomic MnAl Alloys during in-situ TEM Heating Studies.
Jorg M. K. Wiezorek[1], Cagatay Yanar[2], Eric Stach[3], Velemir Radmilovic[4] and William Soffa[5]; [1]MSE, University of Pittsburgh, Pittsburgh, Pennsylvania; [2]Alcoa Technical Center, Alcoa Center, Pennsylvania; [3]Purdue University, West Lafayette, Indiana; [4]NCEM - LBNL, Berkeley, California; [5]MSE, University of Virginia, Charlottesville, Virginia.

The Mn-Al-base ferromagnetic alloys derive their attractive combination of magnetic properties from the formation of a ferromagnetic tetragonal L1o-ordered tau-phase that exhibits a strong uniaxial magnetocrystalline anisotropy. During heat treatment and thermomechanical processing the tetragonal tau-phase forms primarily through a massive transformation from a disordered hcp parent phase. However, a competing mode of formation has been identified by several investigations, generally in conjunction with a secondary B19 ordering reaction, which produces a mophologically plate-like product. Hence, this mode of phase transformation is often referred to as the shear or displacive mode of tau-phase formation. Here the nature of this shear mode for tau-phase formation has been characterized using post-mortem TEM and in-situ TEM heating experiments. The in-situ TEM studies revealed a synergistic relationship of the shear mode to the massive transformation. Combinations of dynamic in-situ TEM hot stage experiments and post-mortem TEM studies have enabled observations of the shear mode dynamics and all relevant crystallographic detail. Its synergistic relationship to the massive transformation and B19 ordering will be discussed. The implications of this complex reaction mechanism will be elaborated upon regarding evolution of defect structures in MnAl. Support from the National Science Foundation (DMR-Metals) is gratefully acknowledged.

9:15 AM MM5.4
***In-situ* HREM Observation of Phase Transformation Process of FePt and FePtCu Nanoparticles by Specimen-heating Holder.**
Masatoshi Nakanishi[1,3], Genichi Furusawa[1], Koukichi Waki[1], Yasushi Hattori[1], Takeo Kamino[2], Katsuhiro Sasaki[3], Kotaro Kuroda[3] and Hiroyasu Saka[3]; [1]Fuji Photo Film Co., Ltd., Minamiashigara Kanagawa, Japan; [2]Hitachi Science System Ltd., Hitachinaka Ibaraki, Japan; [3]Nagoya University, Nagoya Aichi, Japan.

The phase transformation process of individual FePt and FePtCu nanoparticles synthesized by the reverse micelle method has been investigated by the *in-situ* HREM observation using a specimen-heating holder in FE-TEM. The polycrystalline FePt particles were reconstructed into single crystals of chemically disordered face-centered cubic phase (A1) at 650 °C. The phase transformation of FePt particle from A1 to chemically ordered face-centered tetragonal phase ($L1_0$) was induced at 680 °C. The critical temperature of single crystal formation and the phase transformation temperature of the FePtCu nanoparticles were 500 °C and 600 °C, respectively, which were lower than those of the FePt nanoparticles. Coalescence process began at the phase transformation temperature as a result of ferromagnetism of emerging $L1_0$ phase. The addition of Cu lowered the temperature of phase transformation from metastable A1 to equilibrium state $L1_0$, increasing the atomic diffusivity, thereby enhancing the kinetics of ordering.

9:30 AM *MM5.5
In-situ TEM Methods for Characterizing the Behavior of Partially Molten Al-Si Alloy Nanoparticles.
James M. Howe[1], Vladimir P. Oleshko[1], Santhana K. Eswaramoorthy[1] and Takeshi Yokota[2]; [1]Materials Science & Engineering, University of Virginia, Charlottesville, Virginia; [2]Steel Research Laboratory, JFE Steel Corporation, Kawasaki, Japan.

In-situ transmission electron microscopy (TEM) is an indispensable tool for characterizing and manipulating nanomaterials under various experimental conditions. Experiments utilizing liquid phases present some unique challenges for TEM, but also offer possibilities to explore interesting phenomena that do not occur in solids. This presentation illustrates how a number of in-situ TEM techniques have been used to investigate the behavior of solid-liquid interfaces, solid particles in liquids, and the properties of the solid and liquid phases, in Al-Si alloy nanoparticles. A variety of in-situ techniques are discussed, including the use of electron energy-loss spectroscopy and energy filtering TEM to determine the dielectric and other physical properties of the solid and liquid phases and the compositional changes across the solid-liquid interface, respectively, the effects of electron irradiation on the melting behavior of the nanoparticles and motion of a solid Al-rich sphere inside liquid Al-Si alloy, the use of the electron beam as "electron tweezers" to steer the solid Al sphere in the liquid Al-Si, the use of a calibrated heating holder to determine the mechanisms and kinetics of solid-liquid interface motion during solidification, as well as a newly developed thermal shield for commercial TEM holders that allows one to perform energy-dispersive X-ray spectroscopy at significantly higher temperatures than is usually possible. This research was supported by the National Science Foundation under Grant DMR-9908855 and the Department of Energy under Grant DE-FG02-01ER45918.

SESSION MM6: Annealing/Grain Growth
Chair: RC Pond
Tuesday Morning, November 29, 2005
Hampton (Sheraton)

10:30 AM *MM6.1
In situ TEM investigation of Abnormal Grain Growth in

Nanocrystalline Ni. David M. Follstaedt[1], Khalid Hattar[2], James A. Knapp[1] and Ian Robertson[2]; [1]Dept. 1111, Sandia National Laboratories, Albuquerque, New Mexico; [2]Materials Science & Engineering, University of Illinois, Urbana, Illinois.

Pulsed-laser deposited Ni has several features that allow the intrinsic properties of a nanocrystalline (ncr) metal to be examined: high purity, no detectable porosity, and grain sizes down to 10 nm. The energy stored in the dense network of grain boundaries in this ncr Ni can promote the formation of larger grains, given sufficient atomic motion. It is important to determine the limits of thermal stability of ncr Ni because it is being used to develop miniature components for microsystems, and grain growth would alter their mechanical properties. We have used transmission electron microscopy (TEM) at 200 or 300kV to investigate the grain growth during thermal treatment. Specimens were prepared by depositing 150 nm of Ni onto a [100] surface of NaCl, gluing a Cu grid to the film and then dissolving the salt away in water, or by deposition onto silica and backthinning. The films consisted of randomly oriented fcc Ni with grain size ∼20nm. In situ heating stages were used to examine the films during annealing. We readily observed abnormal grain growth at about 300C by bright-field video microscopy. Growing grains appeared as white areas that were not strongly diffracting; they usually do not exhibit a high-symmetry orientation with respect to the film surface. We could directly observe nanocrystalline grains being engulfed and nearby grains growing into each other. We observed grain growth at a temperature as low as 225C after 14 hours, with most of the film still in the ncr state. Notably, grain growth was enhanced by a 200 kV electron beam; when heated specimen areas not previously examined were investigated, much less abnormal grain growth was seen. Post-mortem TEM examination using tilting and diffraction contrast of a film annealed at 275C showed three general types of grains having: 1) high-angle internal boundaries, 2) twin boundaries, and 3) misorientation with slowly changing contrast across the grain. The high-angle boundaries (1) apparently formed when two or three nearby abnormal grains grew into each other. The twin boundaries (2) may indicate a special type of growth initiation between two adjacent grains with this low-energy orientation. The misorientations (3) may have resulted as the growing grain engulfed randomly oriented ncr Ni grains; indeed, some grains showed numerous dislocations that could be associated with the misorientations. Some grains also exhibited stacking fault tetrahedra, suggesting that vacancies were released into the grain when it grew into the ncr Ni with its high density of grain boundaries. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energys National Nuclear Security Administration under contract DE-AC04-94AL85000.

11:00 AM MM6.2
On the Mechanism of Resistive Switching in MIM Capacitors – An Approach with In-situ TEM Experiments.
Herbert Schroeder, IEM am IFF and cni, Forschungszentrum Juelich GmbH, Juelich, Germany.

Simple, non-volatile memory devices such as switchable resistors are desirable for future ultra-large scale-integrated memory chips in cross-bar architecture. A large variety of candidates is presently under discussion such as magnetic RAM, phase change materials, single molecules, polymers and other organic insulating materials, and ferroelectric and paraelectric oxides. There are numerous experimental (leakage) current data published in the literature for each material class demonstrating the switchable memory effect but there is no agreement on the working mechanism, especially for the oxides. To a large extent this is due to the lack of microstructural information on the changes during formation and switching of the devices. Among the suggested mechanisms the creation and destruction of high-conductive paths, so-called filaments, is favored by many groups. If these effects are connected with microstructural changes it may be observable in a TEM. In this contribution an in-situ TEM experiment is suggested to observe the microstructure of a metal/insulator/metal (MIM) capacitor structure during resistive switching due to an applied external voltage or current. For this experiment a special TEM sample holder has been developed allowing controlled in-situ application of temperature (RT to 300C°)with a heating stage and of voltage (current) as a part of a 4-point resistance measurement set-up. This is combined with a special TEM sample preparation method, the so-called window-technique, for which the silicon substrate is etched away from the backside, so that no thinning of the MIM thin film structure is necessary at all (which is an advantage as the oxides are known to be very sensitive to damage introduced by methods such as ion-milling). Special electrode configurations have been designed to allow nearly undisturbed TEM observation of insulator. Identical samples are also investigated ex-situ in conventional switching experiments to identify the influence of the special TEM environment (high vacuum, irradiation with energetic electrons). Examples for first observations are presented as well.

11:15 AM MM6.3
Mechanisms of Grain Growth in Nanograined Metallic Structures. Jennifer A. Gregg, Khalid Hattar and Ian M. Robertson; Material Science and Engineering, University of Illinois, Urbana, Illinois.

Retention of the enhanced properties reported for nanograined metallic systems requires that the nanostructure by insensitive to temperature and deformation. We have employed in-situ TEM annealing technique to investigate the structural and chemical changes associated with the formation of micron-sized grains from nanograined evaporated gold and copper thin films. The grain growth occurs randomly throughout the films in both materials. Twinning but not dislocation slip occurs in the growing grains until the grain size is in the hundreds of nanometer range. The twins grow with the grains in copper but in gold they appear to inhibit growth and must be annihilated before growth can continue. These differences are considered in terms of the impurity content of the films, both in the grain and on the grain boundary, and on the depth of the grain boundary grooving as a function of film thickness. The observed grain growth mechanisms will be compared with recent molecular dynamics computer simulations and with predictions from grain growth theory.

11:30 AM MM6.4
In-situ and ex-situ TEM Study of Morphological Change of Ba(NO3)2 Supported on gamma-Al2O3 and alpha-Al2O3(0001) upon Heating. Chongmin Wang[1], Ja Hun Kwak[1], Do Heui Kim[1], Janos Szanyi[1], R. Sharma[2], S. Thevuthasan[1] and Charles H. F. Peden[1]; [1]Pacific Northwest National Laboratory, RIchland, Washington; [2]Arizona State University, Tempe, Arizona.

One of the key challenges faces the catalysis community is the elimination of harmful gases emitted by internal combustion engines. In particular, the reduction of NOx from an exhaust gas mixture that contains an excess amount of oxygen is difficult. One of the most promising technologies under consideration is the NOx storage/reduction (NSR) method. This process is based on the ability of certain oxides, in particular alkaline and alkaline earth oxide materials, to store NOx under lean conditions and release it in rich (excess reductant) engine operation cycles. The most extensively studied catalyst systems for this purpose are based on BaO supported on Al2O3. During the NOx uptake the BaO/BaCO3 phase is converted to Ba(NO3)2 which, in turn, releases NOx in the rich cycle and reforms the active NOx storage phase of BaO. One key issue to be addressed is the morphological change of Ba(NO3)2 to BaO upon heating for releasing of NOx or vis versa from BaO to Ba(NO3)2 upon uptaking of NOx. In this presentation, we report our in-situ and ex-situ TEM study of above catalyst system. Two types of supporting materials were chosen. One is the ?-alumina powder particles, and the other is the thin section of single crystal ?-Al2O3. Both in-situ and ex-situ TEM results are compared with the results obtained based on IR, TPD, and 15N solid state NMR.

11:45 AM MM6.5
In Situ Recrystallization Imaging of Polycrystalline Ni-S Alloy by SEM. Marilyne Cornen and Rene Le Gall; LGMPA, Polytech'Nantes, Nantes cedex 03, France.

Impurity segregation at alloy grain boundaries (GB) depends on many parameters such as GB character and prior thermomechanical history. In this paper we describe an experimental set-up designed to record the individual behaviour of GB during recrystallization of a Nickel-Sulphur alloy. The aim is to correlate segregation level with mobility and disorientation of GB. Therefore a method allowing direct observation of the GB motion as well as disorientation mapping is needed. Studying grain growth and recrystallization of this particular alloy by Scanning Electron Microscopy is possible thanks to real time in-situ imaging. This requires a sensitive crystal orientation contrast and the ability to image hot evolving samples. To heat the samples, a special device designed for the SEM analysis chamber is used. It consists of a small sample welded on a tantalum foil and heated by conduction through two pieces of copper. A very thin thermocouple is placed at one end of the sample. Heating is controlled using a fast controller combined with a high response power supply. This device is used at 455 degrees Celsius but is able to reach higher temperatures. In order to get the orientation contrast images, as well as to protect the Secondary Electron (SE) detector from heat and light, we have built a channel plate converter. This channel plate consists of a titanium box coated with a high SE yield material (magnesia) placed over the heating device. The backscattered electrons striking the plate generate additional secondary electrons. A small hole is provided for the beam to reach the sample and another one near the bottom of the box lets secondary electrons to pass through to the SE detector. Thanks to this experimental set-up, combined with the heating system, we can observe the sample during recrystallization and get small videos providing information such as grain boundary mobility. Then associated with an EBSD analysis we can get the disorientation

map of the area of interest and eventually an electrochemical technique is performed to create preferential dissolution at GB. Geometry of the grooves created through electrochemical etching gives a valuation of the segregation level in GB.

SESSION MM7: Nanomaterials I
Chair: Zhong Wang
Tuesday Afternoon, November 29, 2005
Hampton (Sheraton)

1:30 PM *MM7.1
In Situ HREM Study on High Temperature Behavior of Nanometer-Sized Silver Particles on Graphite. Junggoo Lee and Hirotaro Mori; Research Center for Ultra High Voltage Electron Microscopy, Osaka University, Suita, Osaka, Japan.

It is now well established that nanometer-sized particles exhibit phase stabili-ties that is different from those of the corresponding bulk materials. The establishment is appreciably owing to the rapid progress in high resolution electron microscopy (HREM), which enabled us to study the phase change in nanometer-sized particles in an atomic scale. Most of HREM studies on the phase change, however, have been concerned with the confirmation of such phase tran-sitions as the solid-to-liquid transition. To the authors' knowledge, HREM obser-vations on the solid-to-gas transition (i.e., sublimation) are rare although it is of significance to directly confirm whether a nanometer-sized particle on a substrate would undergo a solid-to-gas transition until whole the particle disappear or a par-ticle would first undergo a solid-to-liquid (i.e. melting) transition and then un-dergo a liquid-to-gas transition until all the constituent atoms of the particle would evaporate. In the present work, a series of in-situ HREM experiments have been carried out to study the atomic process of solid-to-gas transition in nanometer-sized silver particles on a graphite substrate. Nanometer-sized silver particles were prepared on a graphite substrate using a side-entry holder which was equipped with an evaporator at its tip, in a Hitachi HF-2000 type 200kV HREM. The particles were then subjected to in-situ anneal-ing experiments in the microscope. Heating resulted in sublimation of silver at-oms from crystalline silver particles under the vacuum of 7E-7 Pa and subse-quent size reduction of the particles. The rate of sublimation-induced radius change of the particles was approximately 0.024nm/s at 800K. The sublimation continued until whole the silver particles disappeared. Melting of the particles, however, did not occur during this process. In addition, multiply twinned particles (MTPs) changed into single crystalline particles when the size was reduced down to approximately 6-7 nanometers in diameter during the sublimation. It was also confirmed that the height-to-width ratio of a single crystalline silver particle on graphite at 800K was almost 0.65, and the ratio did not change so much during the sublimation-induced shrinkage of the particle. Based upon these results, high temperature behavior of nanometer-sized silver particles supported on graphite will be discussed.

2:00 PM MM7.2
UV-FEL Photo-Electron Emission Microscopy of $TiSi_2$ nanostructure dynamics on Si (100). Matthew C. Zeman[1], W. -C. Yang[2,1] and R. J. Nemanich[1]; [1]Physics, North Carolina State University, Raleigh, North Carolina; [2]Physics, Dongguk University, Seoul, South Korea.

The coarsening dynamics of nanoscale titanium disilicide ($TiSi_2$) island and wire structures are observed using tunable ultra-violet free electron laser (UV-FEL) excitation for a photo-electron emission microscope (PEEM). The UV-FEL PEEM is employed for $in-situ$, $real-time$ observation of the nanostructures at temperatures ranging from room temperature to 1150^{o}C. The nanostructures are prepared in-situ by depositing a thin Ti layer on a clean Si (100) surface. The samples are then annealed to $\sim$950^{o}C, during which we observe the formation of $TiSi_2$ nanostructures that are clustered into domains on the surface; some of which contain nanoscale islands and others that contain nanowires. Further annealing to 1150^{o}C results in the coarsening of the nanostructures via Ostwald ripening (OR) and coalescence. In the areas of the surface containing islands we observe significant OR as well as islands that migrate attractively towards each other and subsequently coalescence. In the regions that contain wires we observe structures which attractively coalesce as well as wires that shrink from both ends and ripen away.

2:15 PM MM7.3
Linear Atomic Suspended Metallic Chains From HRTEM Experiments. Fernando Sato[1,3], Pablo Z. Coura[2], Socrates O. Dantas[2], Sergio B. Legoas[3], Varlei Rodrigues[1,4], Daniel Ugarte[1,4] and Douglas S. Galvao[1]; [1]Applied Physics, State University of Campinas, Campinas, Sao Paulo, Brazil; [2]Physics Department, Federal University of Juiz de Fora, Juiz de Fora, Minas Gerais, Brazil; [3]Physics Department, Federal University of Amazonas, Manaus, Amazonas, Brazil; [4]Laboratorio Nacional de Luz Sincrotron, Campinas, Sao Paulo, Brazil.

Metallic Nanowires (NWs) have been object of intense experimental and theoretical investigations in the last years. A considerable effort has been devoted to understand the structural and conductance properties of NWs and suspended chains at nanoscale. From experimental point of view two techniques have been mostly used, mechanically controllable break junctions and in situ high resolution transmission electron microscopy (HRTEM). The former is more appropriate for conductance experiments while the latter allows real time visualization, providing a better evaluation of the dynamical aspects of NW elongation. Details about the mechanisms of NWs formation, structural stability and transport properties are still not completely understood. Although most of the work on NWs has been focused on gold, in contrast with some theoretical predictions, other fcc metals have experimentally produced linear atomic suspended chains (LACs). In this work we report experimental HRTEM and theoretical molecular dynamics results of LAC formation for gold, silver, cooper and platinum. Experimentally, metallic nanowires are generated in situ - HRTEM (JEM 3010 URP, 300 kV, 0.17 nm resolution, at LME/LNLS Campinas, Brazil) - using the method developed by Takayanagi' group. The microscope electron beam (current density 100 A/cm.cm) is focused on a self-supported polycrystalline metallic thin film (5 nm thick, deposited on a holey carbon grid) to drill holes at different sites until nanometric bridges are formed between neighboring holes. These holes evolve spontaneously sometimes to form LACs. The molecular dynamics simulations were carried out using a tight binding methodology using second moment approximation (SMA) with a small set of adjustable parameters. This methodology allows us to incorporate the statistical aspects of the experimental conditions as well as to address the temporal evolution of the NWs under mechanical stretching. We have observed the formation of remarkable structures, in terms of structural features and stability for all the studied metals. The LAC formation has also been observed for all of them. Our results show that different initial crystallographic orientations lead to very differentiated LAC formations and strongly support that kinetic aspects are the dominant mechanisms determining the LAC morphologies.

SESSION MM8: Nanomaterials II
Chair: Hirotaro Mori
Tuesday Afternoon, November 29, 2005
Hampton (Sheraton)

3:30 PM *MM8.1
Nano-Scale Property Measurments of Individual Nanotube/Nanowire by in-situ TEM. Zhong L. Wang[1], Xuedong Bai[2], Zhi Xu[2] and Enge Wang[2]; [1]School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia; [2]International Center for Quantum Structure, Institute of Physics, CAS, Beijing, China.

Characterizing the physical properties of individual nanostructures is rather challenging because of the difficulty in manipulating the objects of sizes from nanometer to micrometer. Most of the nanomeasurements have been carried using STM and AFM. In this presentation, we demonstrate that transmission electron microscopy can be a powerful tool for quantitative measurements the mechanical, field emission and electrical properties of a single nanostructure, such as a carbon nanotube. Using a customer-built specimen holder, in-situ measurements on the mechanical properties of carbon nanotubes has been carried out using the resonance phenomenon induced by an externally applied alternating voltage [1,2]. The bending modulus of a carbon nanotube was obtained from the resonance frequency at a high precision. Alternatively, a nanotube was demonstrated as a "nanobalance" for measuring the mass of a single nanoparticle in the range of femtograms. The ballistic quantum conductance of a multi-walled carbon nanotube [3] was observed at room temperature using the set up in the TEM. The field emission properties of a single carbon nanotube were observed, and the work function at the nanotube tip was measured [4]. The in-situ TEM technique has also been applied to measure the elastic modulus of SiC-SiO2 composite nanowires [5, 6, 7]. Recently, the field emission at the tip of a single nanotube has been directly correlated to its tip structure. [1] P. Poncharal, Z.L. Wang, D. Ugarte and W.A. de Heer, Science, 283 (1999) 1513. [2] R.P. Gao, Z.L. Wang, Z.G. Bai, W. de Heer, L. Dai and M. Gao, Phys. Rev. Letts., 85 (2000) 622; Z.L. Wang, P. Poncharal and W.A. De Heer, Pure Appl. Chem. Vol. 72 (2000) 209. [3] S. Frank, P. Poncharal, Z.L. Wang, and W.A. de Heer, Science, 280 (1998) 1744. [4] Ruiping Gao, Zhengwei Pan and Zhong L. Wang, Appl. Phys. Letts., 78 (2001) 1757. [5] Z.L. Wang, Z.R. Dai, Z.G. Bai, R.P. Gao and J.L. Gole, Appl. Phys. Letts., 77 (2000) 3349. J.L. Gole, J.D. Scout, W.L. Rauch and Z.L. Wang, Appl. Phys. Letts., 76 (2000) 2346. [6] Electron Microscopy of Nanotubes, edited by Z.L. Wang, C.

Hui, Kluwer Academic Publisher (2003). [7] Z.L. Wang, New developments in transmission electron microscopy for nanotechnology, Adv. Mater., 15 (2003) 1497-1514. [8] For details: www.nanoscience.gatech.edu/zlwang

4:00 PM MM8.2
Assembly and Interaction of Au/C Core-Shell Nanostructures: In-Situ Observation in a Transmission Electron Microscope. Eli Sutter, Peter Sutter and Yimei Zhu; Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York.

The encapsulation of metals in fullerene cages has attracted much interest recently due to the enormous technological promise and the expected novel and exotic physical, chemical, and electronic properties of encapsulated nanoparticles. Metals such as Co, Ni, Al, and Cu have been encapsulated in carbon fullerene cages via arc discharge processes. Despite the large interest in these nanostructures, the encapsulation process remains poorly understood. Important properties, such as the thermal stability and interactions of encapsulated particles have not been considered. It has been demonstrated that carbon encapsulation can result from intense electron irradiation in a transmission electron microscope (TEM). This finding suggests a route for studying the formation and subsequent interaction and transformation of encapsulated metal nanoparticles via real-time TEM observations. We use electron irradiation in TEM to transform 5 nm Au nanoparticles on C-support into arrays of Au/C core-shell nanoparticles. The formation of the core-shell particles and thermally driven interactions between pure Au and Au/C particles are studied with atomic resolution by real-time in-situ TEM over a temperature range from room temperature to 800 degreesC. Au and Au/C nanoparticles interact by a unique ripening process, which involves the assembly of an atomic Au bridge, and the expansion of this bridge by incorporation of Au atoms diffusing from the individual particles. Fullerene encapsulation initially passivates the Au particles and inhibits such ripening. Ultimately, however, graphene sheets also play an active role and provide a novel mechanical driving force for nanoparticle ripening. On the basis of TEM movies, we discuss Au particle interactions and their modifications by a C-shell, highlighting both the passivation and the extreme environmental conditions induced by fullerene encapsulation.

4:15 PM MM8.3
Atomic scale imaging of wall-by-wall breakdown and concurrent transport measurements in multiwall carbon nanotubes. Jianyu Huang[1], S. Chen[1], S.H. Jo[1], Z. Wang[1], D.X. Han[1], G. Chen[2], M.S. Dresselhaus[2] and Z. F. Ren[1]; [1]Physics, Boston College, Chestnut Hill, Massachusetts; [2]Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; [3]Physics, Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts.

We report the atomic-scale imaging with concurrent transport measurements of the breakdown of individual multiwall carbon nanotubes inside a transmission electron microscope equipped with a piezo manipulator [1]. We found unexpectedly three distinct breakdown sequences, namely, from the outermost wall inward, from the innermost wall outward, and alternatively between the innermost and the outmost walls. Remarkably, a significant amount of current drop was observed when an innermost wall is broken, proving unambiguously that every wall is conducting. Moreover, the breakdown of each wall in any sequence initiates in the middle of the nanotube, not at the contact, proving that the transport is not ballistic. [1] J. Y. Huang, S. Chen, S. H. Jo, Z. Wang, D.X. Han, G. Chen, M.S. Dresselhaus, and Z. F. Ren, Phys. Rev. Lett. 94, 236802 (2005).

4:30 PM MM8.4
In-situ nano-characterization using SPM-TEM holders. Oleg Lourie, [1]Gatan Inc., Pleasanton, California; [2]Nanofactory Instruments AB, Goteborg, Sweden.

The mechanical, electronic and refractive properties of the nanostructures can be studied in TEM using SPM-TEM systems such as STM-TEM and TEM-Nanoindentor holders. Specifically the conductivity, elastic constants and the mechanical strength can be measured with these systems for individual nanostructure such as nanowire or nanotube. Combined with the simultaneous HRTEM imaging and EELS analysis it leads to the full in-situ nano-characterization of the selected nanostructures. In this experiment the individual boron nanowires and boron nitride nanotubes were bent and axially compressed using TEM-Nanoindentor inside the TEM column. The forces generated by the bending and compression of the nanowires were measured along with the deformation imaged by the TEM. The acquired force-deformation data was completed with the EELS characterization. Axial elastic moduli of the boron nitride nanotubes and boron nanowires were also evaluated based on the force-deformation data. Recent experiments with the TEM-STM system have shown that the nanowires can be fragmented as a result of the high density electric current. Using theoretical modeling accounting the thermal and Lorentz forces, the elastic modulus, and axial thermal stress as well as the interfacial properties were evaluated. Based on the EELS data acquired from the boron nanowires and boron nitride nanotubes in this study, the Kramers-Kronig analysis was also used to evaluate the local refractive properties of these nanostructures.

4:45 PM MM8.5
Atom-Resolved Identification of Single & Double-Walled Carbon Nanotubes by HRTEM. Hongwei Zhu[1,2], Kazutomo Suenaga[2], Ayako Hashimoto[2], Bingqing Wei[1] and Sumio Iijima[2]; [1]Department of Electrical & Computer Engineering, Louisiana State University, Baton Rouge, Louisiana; [2]National Institute of Advanced Industrial Science & Technology, Tsukuba, Japan.

One of the challenges during the past couple of years is to visualize the atomic structure and especially, determine their chiralities to high precision. In this presentation, we report a direct access to the atomic structure of individual clean single & double-walled carbon nanotubes (SWNTs & DWNTs) with a higher precision by high-resolution transmission electron microscopy (HRTEM). A specially fabricated high-resolution imaging technique is used to obtain atomic-resolution TEM images of SWNTs and DWNTs. Starting from the optical diffractions (Fourier transformations) of these TEM images, we perform an atom-resolved reconstructing operation in order to get the perfect lattice images of individual tubes. A new approach proposed to accurately determinate tube chiralities involves relevant analysis based on the information of tube diameters/index angles extracted from their optical diffractions and systematic image simulation. It has also been paralleled by an estimation of tube tilting angle with respect to the e-beam direction by iterative comparisons of the experimental results with simulation results. Further, we propose a novel and rational approach to visualize the nucleation points of SWNTs in atomic scale. Both the atomic-structure of the catalysts and tubes growing out were seen by high-resolution transmission electron microscopy (HRTEM) for the first time. The growth pathway extracted from TEM image sequence demonstrates a root mechanism in SWNT growth. We believe that this result represents a significant first step towards in-situ investigating the structure-properties relationship for 1D nano-materials by combining with other characterization techniques.

SESSION MM9: Poster Session
Tuesday Evening, November 29, 2005
8:00 PM
Exhibition Hall D (Hynes)

MM9.1
In Situ TEM Observation of Solid-Gas Reactions at High Temperatures. Keisuke Kishita[1], Takayuki Mima[2], Hiroyasu Saka[2], Kotaro Kuroda[2], Shigeo Arai[2] and Takeo Kamino[3]; [1]Material Engineering Div., Toyota Motor Corporation, Toyota, Aichi, Japan; [2]Graduate School of Engineering, Nagoya University, Nagoya, Aichi, Japan; [3]Naka Application Center, Hitachi High-Technologies, Hitachinaka, Ibaraki, Japan.

A specimen holder equipped with a gas injection nozzle and a heating system has been developed for TEM (Transmission Electron Microscope) observation of solid-gas reactions at high temperatures. Using this specimen holder in a conventional TEM, the gas pressure of the specimen area can be controlled from 10^{-6}Pa to 10^{-2}Pa, and the temperature of the specimen can be controlled from R.T.(room temperature) to approximately 1773K. In this work, we observed in situ oxidation and reduction of Fe_2O_3, Si, etc. with a Hitachi H9000 at 300kV. Phase transition of the Fe system during the oxidation and reduction was observed in a partial pressure of the air ranging from $8x10^{-2}$Pa to $3x10^{-5}$Pa. Phases involved in these reactions were identified using HREM, EELS and EDX. Formation of SiO_2 on Si during the oxidation was dynamically observed in a partial pressure of O_2 ranging from $8x10^{-3}$Pa to $3x10^{-5}$Pa at near atomic resolution.

MM9.2
In-situ TEM Investigation of Structural and Phase Transformations during Solid State Chemical Reactions. Boris Bokhonov and Mikhail Korchagin; Institute of Solid State Chemistry SB RAS, Novosibirsk, Russian Federation.

The key to the understanding of phenomena and reactions that occur during solid-solid interaction lies in the physical and chemical nature of the interphase boundary. Several directions can be separated within this research area: the necessity to develop chemical and physical models of the interface and interphase regions; search for new

experimental data concerning the processes that take place during the formation of phases in solid state chemical reaction; investigation and discovery of the factors determining both the formation of interface and the consequences arising during its movement with the propagation of chemical reaction. For investigation of the mechanisms of interactions of solids, we used the in-situ TEM technique based on direct electron microscopic observation of the transformations that occur with a thin film (amorphous and crystalline) or mono-crystalline foil prepared from one compound and a particle as a second component which has been deposit on the surface of the film. Interaction of solids has been initiated by a special heating unit or by electron beam of increased intensity produced by electron microscope. We chose the next couples of interacting compounds: eutectic composition Silicon/Me (Me=Au,Al, Ag, Cu), the system with unlimited solubility (Au-Cu), the systems in which the formation of intermetallic compounds (Ni-Al and Si-Ni), interaction between amorphous carbon film and metal particles (Fe, Co, Ni). In-situ electron microscopic investigations of the formation of eutectic alloys in the systems: amorphous Si/metal particle showed that the formation of eutectics is preceded by metal diffusion into amorphous silicon with the formation of metastable amorphous metal silicide. Decomposition of the metastable amorphous metal silicide leads to the evolution of polycrystal silicon. An oriented formation of liquid eutectic alloy is observed in the system: crystalline (100)Si/metal particles. In these cases, at the metal-silicon eutectic/silicon crystal interface the formation of silicide phases and dislocation structure is observed. In-situ investigations interaction of nickel particles with single crystalline (100) silicon and amorphous silicon film showed that the sequence of phase formation during the annealing of systems depend on the temperature of interaction. In-situ electron microscopic investigations reaction between Al particle and nickel film demonstrated that the interaction between solids start at temperatures below aluminum melting point and accompanied the formation of intermetallic compound and large number of dislocations. In situ electron microscopic studies of the interaction of metal particles (Fe, Ni, Co) with amorphous carbon thin film showed that the interaction starts at temperatures about 600oC. The interaction in the systems metal/carbon film proceeds via the formation of the carbide phases and their decomposition with the formation of graphite and metal nanoparticles.

MM9.3

High-bias induced structure and electronic property changes in carbon nanotubes. Shuo Chen[1], Jianyu Huang[1], Sung-Ho Jo[1], Ziqiang Wang[1], Krzysztof Kempa[1], Gang Chen[2] and Zhifeng Ren[1]; [1]Department of Physics, Boston College, Chestnut Hill, Massachusetts; [2]Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

High-bias electron transport study conducted concurrently with atomic-scale microstructure observation in individual carbon nanotubes demonstrate that high bias causes significant structure changes to the nanotubes, such as crystallization of amorphous coating on the surface of the nanotube, elimination of the amorphous coating and the nanotube walls, formation of atomic scale kinks. These structural changes alter the electronic property of the nanotubes permanently. The results demonstrate clearly that the permanent electric property change is not caused by the changes of the contact. Our results also provide an effective way to produce DWCNT junctions with controlled conductivity for electronic and electro-mechanical applications.

MM9.4

A Study on the Radiation Damage of Highly Oriented Pyrolytic Graphite (HOPG) by High Resolution High Voltage Electron Microscope. Anjana Asthana[1], Ken-ichi Ohshima[2], Koji Kimoto[1] and Yoshio Matsui[1]; [1]Advanced Materials Laboratory, National Institute for Materials Science, Tsukuba, Ibaraki, Ibaraki, Japan; [2]Institute of Materials Science, University of Tsukuba, Tsukuba, Japan.

A number of reports are found on the structural disordering investigations of the neutron irradiated graphite, graphitized carbon fiber and whiskers by X-ray diffraction and transmission electron microscopy [1-6]. All these studies have revealed the deterioration in the structure of graphite upon irradiation, but could not give a clear model which can explain the mechanism of such dimensional change. In the present study we have tried to investigate the radiation damage of highly oriented pyrolytic graphite (HOPG) crystals by high resolution high voltage electron microscope(operated at 800kV) in order to find a clear model to explain the dimensional change. We have investigated both neutron irradiated and electron irradiated HOPG crystal. Local structure analysis by transmission electron microscopy (TEM) shows that the (0002) lattice spacing for the above-mentioned HOPG samples has been increased by up to 10% for the highest dose of irradiation under the present investigations. This increase in c-axis lattice spacing can be ascribed to the fragmentation of the crystal lattice into nanocrystallites, breaking and bending of the (0002) straight lattice fringes, appearance of dislocation loops and also extra interstitial planes within the fragmented nanocrystallites. All these changes occur due to the static displacement of atoms after neutron irradiation. [1] Kelley B T 1981 Physics of Graphite (London, Applied Sciences) and the references there in. [2] Reynolds W N 1966 Chem. Phys. Graphite 2 121 [3] Zachariasen W H 1945 Classified report [4] Bacon G E andWarren BE 1956Acta Cryst. 9 1029 [5] EELES W T 1968 Acta. Cryst. A 24 688 [6] Tanabe T, Muto S, Gotoh Y andNiwase K 1990 J. Nuc.r Maert. 175 258.

MM9.5

Phase Transitions in $X_2T^1T^2{}_2O_7$ Single Crystals with Modulated Structure. Andreas K. Schaper[1], Zhihong Jia[1,2], Werner Treutmann[1,2], Werner Massa[1,3] and Helmut Rager[1,2]; [1]Material Sciences Center, Philipps University, Marburg, Germany; [2]Department of Geosciences, Philipps University, Marburg, Germany; [3]Department of Chemistry, Philipps University, Marburg, Germany.

While the incommensurability in melilite-type compounds is well-documented [1-3], the underlying atomic configurations and the composition- and temperature-dependent phase behavior are not yet clear till now. Moreover, little is known about the formation of domains and domain boundaries and their interrelation with the two-dimensionally modulated structure. We have prepared single crystal series of the system $(Ca,Sr)_2(Mg,Co,Zn)Si_2O_7$ with systematic isomorphous substitutions on the T^1 and T^2 sites [4]. Using in situ transmission electron microscopy and electron diffraction we have studied the transitions of the incommensurate phase to the high-temperature normal phase (IC-N), which is a second-order transition, and from the incommensurate phase to the low-temperature commensurate lock-in phase (IC-C), which is of first order with pronounced hysteresis behavior. The amplitude and wavelength of the incommensurate modulation were followed at varying composition within the temperature range 90K to 400K. The structural changes involved in the phase transformations occur on different length scales, and show an inhomogeneous evolution throughout the crystal. Octagonal clustering as a possible mechanism of the modulation formation [5] is discussed as well as variations in the microdomain pattern according to varying degrees of internal stress accommodation. Even in the commensurate phase, the clustering of the low-coordinated bundles of T^1 tetrahedra proved not complete. A sawtooth-like periodicity was found related to particular rotations and distortions of the T^1 tetrahedra in the 3 x 3 superstructure. In agreement with recent structure simulations [6], the development of a network of large-scale regular bundles was observed approaching the low-temperature lock-in phase. The space group of the lock-in superstructure was determined by x-ray structure refinement to orthorhombic $P2_12_12$ (compare [7,8]). The work was supported by the German Research Foundation (DFG). [1] F. Roethlisberger, F. Seifert, M. Czank, Eur. J. Mineral. 2 (1990) 585. [2] C. Van Heurck, G. Van Tendeloo, S. Amelinckx, Phys. Chem. Miner. 18 (1992) 441. [3] L. Bindi, P. Bonazzi, M., Dusek, V. Petricek, G. Chapuis, Acta. Cryst. B57 (2001) 739. [4] Z.H. Jia, A.K. Schaper, W. Treutmann, H. Rager, W. Massa, J. Cryst. Growth 273 (2004) 303. [5] M. Riester, H. Boehm, V. Petricek, Z. Kristallogr. 215 (2000) 102. [6] K. Kusaka, K. Hagiya, M. Ohmasa, K. Iishi, Acta. Cryst. B60 (2004) 369. [7] J.D.C. McConnell, Z. Kristallogr. 214 (1999) 457. [8] K. Hagiya, K. Kusaka, M. Ohmasa, K. Iishi, Acta. Cryst. B57 (2001) 271.

MM9.6

Microstructure and Plasticity of Silver/Nickel multilayers. Tobias Karsten Schmidt[1], Patric Gruber[2], Gerhard Dehm[3] and Eduard Arzt[1,2]; [1]Metals Research, Max Planck Institute for Metals Research, Stuttgart, Germany; [2]Physical Metallurgy, University of Stuttgart, Institute for Physical Metallurgy, Stuttgart, Germany; [3]Material Physics, Erich Schmid Institute of Material Science and University of Leoben, Leoben, Austria.

Geometrical dimensions and the presence of interfaces often control mechanical properties of metals in small dimensions. For instance this phenomenon can be used in multilayers to increase the hardness of coatings. In this study, epitaxial Ag/Ni multilayers are analyzed in order to obtain insight in the deformation mechanisms of thin films and multilayers. The Ag/Ni multilayers were grown epitaxially by magnetron sputtering on (111) Si substrates at 300°C. The periodical layer thickness ranged between 100 and 400 nm while the total film thickness was kept constant at 800 nm. The Ag and Ni layers grow with a cube on cube orientation relationship as determined by X-ray diffraction and transmission electron microscopy (TEM). The hardness of the multilayers was measured by nanoindentation and thermal stresses by a laser optical wafer curvature technique. Both nanohardness and biaxial stress at room temperature increase with decreasing layer thickness from 1.05 to 1.53 GPa and from 450 to 700 MPa, respectively. The increase of room temperature stress is consistent with a Hall-Petch relationship. Compared to epitaxial films, plastic deformation of the multilayers begins at higher temperatures

(above 350°C) and higher compressive stresses (around 300 MPa). TEM studies are formed to analyze the dislocation mechanisms causing the size effect.

MM9.7
HAADF-STEM and EELS Characterization of Carbon Nanosphere and Silver Nanoparticles Composites.
Xiaoxia Gao[1], Roman Caudillo[1], Jose Luis Elechiguerra[2] and Miguel Jose Yacaman[2,1,3]; [1]Texas Materials Institute and Materials Science & Engineering, The University of Texas, Austin, Austin, Texas; [2]Department of Chemical Engineering, The University of Texas, Austin, Austin, Texas; [3]Advanced Materials Research Center, The University of Texas, Austin, Texas.

This paper presents a study of using HRTEM,HAADF-STEM and EELS to characterize the physical and chemical bonding of carbon silver nanoparticle composites. Nanocomposites were prepared by the pulsed high power plasma arc-discharge between two Ag electrodes in acetylene gas. The TEM characterization shows that the nanocomposites consist of silver nanoparticles encapsulated in carbon nanospheres, which are connected to form necklace-like structures. It was found that silver nanoparticles could be removed from the carbon nanospheres with electron beam irradiation, which clearly reveals that their structures consist of spherical carbon cages with average size 10 nm. The EELS spectrums show the presence of sp1, sp2 and sp3 hybridized carbon, with sp2 character dominating. Based on HRTEM, STEM images, in addition to EELS data, we proposed a large fullerene-like open structure containing defects with sp1 character.

MM9.8
In-Situ Study of Discontinuous Precipitation in Al-22 at.% Zn. Guillermo Solorzano, Materials Science and Engineering, PUC-Rio de Janeiro, Rio de Janeiro, RJ, Brazil.

In the present study, attention was focused on in-situ work on discontinuous precipitation phenomena in Al-22 at.% Zn in a high voltage electron microscope using a hot stage and a video recording system. The microscope was AEI instrument with a maximum voltage of 1.25 MV. The voltage use was 500 kV. The scope of the present study was two folds: first to observe the behavior of individual grain boundaries acting as reaction front of the discontinuous precipitation; second, to check if the grain boundary migration during the discontinuous precipitation reaction proceeds with constant velocity or in a stop-and-go fashion. It was observed and documented that the extent of the discontinuous reaction is dependent on the individual structural characteristics of the grain boundary leading the growth process. While some high angle boundaries, after a given annealing time, are able to migrate and generate well- defined lamellar colonies before ceasing migration, some high mobility boundaries completely consume the original grain upon migration until reaching another boundary and proceed backwards migration, however coarsening the discontinuous precipitation colonies. On the other hand, it has been clearly documented and demonstrated that reaction front migration during discontinuous precipitation occurs in a stop-and-go fashion. Consequently, there is a drastic difference between the average velocity and the instantaneous velocity. This is an important information for our understanding of the kinetics behavior of this reaction and for the choice of the right model description.

MM9.9
In situ Structural Phase Transition Analysis in Doped Strontium Titanate. Paula Maria Vilarinho[1], Alexander Tkach[1], Andrei Kholkin[1], Ian M. Reaney[2], Jan Pokorny[3] and Jan Petzelt[3]; [1]Department of Ceramics and Glass Engineering, University of Aveiro, Aveiro, Portugal; [2]Department of Engineering Materials, University of Sheffield, Sheffield, United Kingdom; [3]Department of Dielectrics, Institute of Physics, Czech Academy of Sciences, Prague, Czech Republic.

Strontium titanate (ST) is used as a substrate for superconducting quantum interference device (SQUID) applications. It serves as a resonator for radio-frequency SQUID operations, improving the stability of the operating point at 77 K. On cooling to this temperature, ST is known to undergo a structural phase transition (SPT) from a high-temperature cubic to a low-temperature tetragonal centrosymmetric phase with a doubling of the unit cell, associated with rotations of the oxygen octahedra around one of the <100> axes. This transition permits the formation of ferroelastic domains and antiphase boundaries which may affect the resonator properties. Thus, there is interest in the study of the SPT in ST and ways to control it. The simplest way to investigate structural transformations in perovskite type materials which undergo oxygen octahedral tilt transitions is to observe the superlattice reflections which appear on cooling. X-ray diffraction is largely insensitive to scattering from the oxygen sublattice and therefore it is difficult to detect the SPT. Furthermore, distortion of the cation sublattice is often quite small and the associated peak splitting may be difficult to observe. Neutrons diffract strongly from oxygen but this method of measurement is not widely available. On the other hand electron diffraction (ED) within the transmission electron microscope is widely available and electrons scatter from the oxygen superlattice with sufficient strength to form discrete reflections. The major disadvantage is that the intensity of each reflection cannot be quantified. Qualitative estimates can be made, however, provided that the exposure times for each negative are not significantly different. Therefore, the onset of the phase transitions and the nature of the tilting can be identified by electron diffraction. Raman spectroscopy is another powerful tool for the characterization of the lattice dynamic of materials that can be used in parallel with ED in order to characterise the SPT. The tendency to lattice instability and SPT are revealed by the decrease in some peak frequencies (mode softening). In this work, in situ cold-stage ED / TEM and Raman spectroscopy were used to study the structural phase transition of ST ceramics doped with Mn, Mg, Bi, La and Cr. The temperature of the SPT T_a was found to increase considerably with doping on the Sr site, while a shift of the SPT to lower temperatures was observed for the doping on the Ti site. For Sr-site doped ST ceramics, $<110>_p$ zone axis ED patterns revealed 1/2{odd-odd-odd} superlattice reflections and the Raman spectra revealed the presence of modes from the R-point of the Brillouin zone, each being a feature of antiphase octahedral rotations much above the T_a ≈108 K of undoped ST. For Ti-site doped ST ceramics, 1/2{odd-odd-odd} discrete superlattice reflections were observed in <110> ED patterns only at 16 K, while at 80 K both superlattice reflections and R-modes were almost undetectable.

MM9.10
Structural information from dose-dependent EELS in CaAl2O4. Nan Jiang, Physics, Arizona State University, Tempe, Arizona.

Electrostatic field-enhanced migration of ions in oxide glasses and crystals has been intensively observed in scanning transmission electron microscopy (STEM). In this case, excitation by fast electrons causes that some electrons in the atoms are driven out of the trajectory of the beam. The trajectory region thus becomes charged positively and positive ions are repelled from its vicinity. The dynamics of ion migration can be directly observed using dose-dependent EELS (DDEELS) technique, which has been able to reveal a wealth of information about electronic and atomic structure, and chemistry of interaction region. Here, we demonstrate that DDEELS technique can also play an important role in the study of glass structures. DDEELS of O K-edge, as well as Al and Ca L23-edges, in crystalline CaAl2O4 were obtained. The spectra are interpreted with the aid of electronic structure calculations. In short, we found that nearly half amount of Ca still remains in the irradiated region after rearrangement of O ceases (i.e. the change of O K-edge stops), and the threshold of O K-edge shifts upwards about 0.5eV. In CaAl2O4, two third Ca is 6-fold coordination Ca(6) and one third is 9-fold Ca(9). Correspondingly, O can also be categorized into three groups: O[Ca(6)] is bound to Ca(6) only, O[Ca(9)] is bound to Ca(9) only and the others are bound to both. (Each O atom is also bound to two Al.) The calculations of density of states (DOS) projected on two different types of Ca and O show that the threshold of the total DOS on Ca(9) is about 0.5eV lower than that on Ca(6). Correspondingly, the threshold of O p-DOS on O[Ca(9)] is also about 0.5eV lower than that on O[Ca(6)]. Therefore, we can assign the threshold intensity of O K-edge to the oxygen that is bound to 9-fold coordinated Ca. Eliminating this type of oxygen is associated with the repulsion of Ca(9) by electrostatic field. In conclusion, the 9-fold Ca can be repelled more easily than the 6-fold Ca. This criterion has been extended to glasses to identify cation coordination, which is crucial to the measurement of medium-range order in glasses. This work is supported by the NSF Grant No. DMR-0245702.

MM9.11
In-Situ Microscopy of the Oxidation of Ru(0001). Peter Sutter, Jan Hrbek and Robert Q Hwang; Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York.

The oxidation of Ru(0001), leading to the formation of a monolayer thick rutile RuO_2(110) surface oxide, has attracted significant research interest recently. RuO_2(110)/Ru(0001) is an exceptional CO oxidation catalyst,[1] and has been studied in the context of a variety of other oxidation reactions.[2] While catalytic reactions on RuO_2(110)/Ru(0001) have been considered in detail, the atomic-scale oxidation pathway of Ru(0001) leading to the formation of RuO_2(110) remains poorly understood. In-situ microscopy of the Ru surface during oxidation has the potential of identifying the atomistic oxidation mechanism and the rate-limiting step of the reaction, and should clarify the role of sub-surface oxygen phases thought to be an integral part of the oxidation process.[3] Using dynamic observations by low-energy electron microscopy (LEEM) with high spatial and temporal resolution, we study the nucleation, growth, and coalescence of RuO_2(110) on Ru(0001). Exposure to NO_2 as the oxygen-carrying

precursor over a range of sample temperatures shows step edges as preferred sites for the initial nucleation of RuO_2 at low temperature, while homogeneous nucleation is observed at higher temperatures. By analyzing the growth of individual RuO_2 nuclei in LEEM movies as a function of temperature and of their local environment (i.e., in the presence of other nuclei, of surface defects and steps) we discuss the microscopic processes involved in RuO_2 formation and compare our findings with atomistic theoretical models proposed to describe the oxidation reaction.[3] 1 H. Over et al., Science **287**, 1474 (2000). 2 Y. Wang, K. Jacobi, and G. Ertl, J. Phys. Chem. B **107**, 13918 (2003); U.A. Paulus, Y. Wang, H.P. Bonzel, K. Jacobi, and G. Ertl, J. Phys. Chem B **109**, 2139 (2005). 3 K. Reuter, M. V. Ganguglia-Pirovano, C. Stampfl, and M. Scheffler, Phys. Rev. B **65**, 165403 (2000).

MM9.12
In-Situ Observation of Thickening of Oxide-Layer in Fe-Iron Oxide Core-Shell Structured Nanoparticles under Electron Beam Irradiation. Chongmin Wang[1], Donald R. Baer[1], JiJi Antony[2] and You Qiang[2]; [1]Pacific Northwest National Laboratory, RIchland, Washington; [2]Physics, University of Idaho, Moscow, Idaho.

Iron nanoparticles have been found to be very effective for removing environmental contaminants in water. However, it is known that a pristine surface of Fe0 exposed to air or oxygen-including atmosphere is oxidized instantly, a process normally called initial oxidation. On a very broad basis, oxidation behavior of iron is highly dependent on factors such as temperature, oxygen partial pressure, and time, all having an influence on the overall oxide layer thickness. High temperature thickening of oxide layer on metal surface is very well understood based on intensive experimental work and thorough theoretical derivations. Contrasted with the understanding of high temperature growth of thick oxide layer, less is known about the initial oxidation process of iron and the structural nature of their product. Under the framework of the Caberra-Mott theory of oxidation of metal, the initial oxidation process of iron can be described as the following: upon initial attachment of oxygen onto the surface of metal and formation of a thin layer of oxide, electron tunnels through the thin oxide layer and ionizes the oxygen, leading to an electrical field between the metal and the surface of the oxide layer. The electrical field will subsequently drive the outwards diffusion of the ionized Fe. With the Caberra-Mott model, estimation has given that at room temperature, it takes about 0.2 femto second to form an initial 1 nm thickness of oxide layer on a freshly exposed iron surface, and 40 seconds for a film of 2 nm, 40 weeks for a film of 3 nm, and 600 years for a film of 4 nm. Recently we have synthesized Fe nanoparticles with a range of size and controlled oxidizing of those nano particles lead to a passivation of the surface layer. It has been observed that under electron beam irradiation in a HRTEM imaging, core-shell structured Fe/iron oxide nanoparticles show in-situ thickening of the oxide shell, typically from $\sim$ 3 nm to 6 nm. This observation provides direct evidence on the Mott theory on initial oxidation. Implications of these observation is also discussed

MM9.13
Cryo-Electron Microscopy and Spectroscopy of Solvated Nafion. Sergey Yakovlev, Alioscka Sousa and Matthew R. Libera; CBME Dept., Stevens Institute of Technology, Hoboken, New Jersey.

Nafion is a perfluorinated ionomer which was developed over forty years ago and about which there remain ongoing arguments concerning its structure. Because of its sulfonate groups, it can absorb substantial amounts of water and is often used as a membrane material in fuel cell applications and in perm-selective clothing applications where moisture and air must be allowed to pass while toxic substances must be blocked. Dissolved solvents are known to play a key role in determining many important properties of Nafion, and, while there are many techniques available for determining the total amount of solvent averaged over an entire macroscopic specimen, few methods are available for studying the spatial distribution of solvents at nano and micro length scales over which many elements of polymer morphology such as phase separation and crystallinity vary. In response, we are developing methods based on spatially-resolved electron energy loss spectroscopy (EELS) to map solvent distributions in synthetic polymers. Unlike electron microscope studies of most inorganic materials where resolution is limited by the aberrations of the imaging system, solvated polymers are extremely radiation sensitive. In this case, spatial resolution is dose-limited and determined by a material's radiation response. Hence we carefully characterize spectroscopic changes as a function of irradiation conditions in the microscope. To work with solvated materials we use cryogenic specimen preparation, cryotransfer into the microscope, and in-situ cryo-imaging and analysis. We use scanning transmission electron microscopy combined with EELS to localize regions of high solvent concentration. In order to make the most efficient use of the incident electron dose, we use the low-loss portion of the EELS spectrum where the scattering cross sections are highest. We have measured the dose-dependent spectral changes of dry Nafion, hydrated nafion, and Nafion fully solvated with Dimethyl methyl phosphonate (DMMP). Significantly, low-loss spectra of pure Nafion, pure amorphous ice, and pure amorphous DMMP are all distinguishable from each other. Multiple least squares fitting of experimental spectra from hydrated Nafion finds average water concentrations in good agreement with values given by weight-gain measurements. We find that pure dry Nafion is extremely sensitive to 200 keV ionizing electron irradiation and exhibits significant mass loss under the electron beam. Significantly, that sensitivity decreases when Nafion is hydrated or solvated with DMMP. This finding is in contrast to the behavior of most hydrocarbon polymers which become more radiation sensitive in the presence of water. Our ongoing studies take advantage of a newly upgraded energy-loss spectrometer that should increase the effective quantum detective efficiency in spectrum-imaging mode to increase the dose-limited resolution of our microscope by a factor of approximately three times.

MM9.14
Abstract Withdrawn

MM9.15
Scanning Electron Microscopy In-Situ Tensile Deformation Observations of Structural Alloys. Carl Joseph Boehlert, Chemical Engineering and Materials Science, Michigan State University, East Lansing, Michigan.

Scanning electron microscopy (SEM) characterization was performed during tensile deformation of high-temperature structural alloys including Inconel Alloy 718 and titanium-aluminum-niobium (Ti-Al-Nb) alloys in order to characterize and understand their deformation evolution. The stress-strain relationship was obtained using an Ernest F. Fullam, Inc. tension stage which allowed for testing at temperatures ranging between 25-800C and loads up to 1000 pounds within the SEM (either an FEI XL-30 or CAMSCAN44FE) chamber. The sample was tilted 70 degrees within the chamber to obtain electron backscattered diffraction (EBSD) maps prior to and after deformation. The surface deformation behavior was characterized prior to global yielding and after global yielding of the sample and a tensile stress versus strain plot was acquired during the experiments. The specimens were imaged at strain intervals between 0.7% and 7.5% global strain. For Inconel Alloy 718, local slip occurred prior to global yielding and after global yielding the surface exhibited extensive slip deformation as slip traces accumulated within the grains. Cracking was exhibited within the Nb-rich precipitates. A 10% cold rolled (CR) specimen exhibited similar room-temperature strength, approximately 1400MPa, as that for a 0%CR specimen. Both the as-rolled and 10%CR specimens exhibited a ductile response and their elongation-to-failure values were more than 7%. Strain was observed to be relatively homogeneous throughout the reduced-area gage section. The Ti-15Al-33Nb(at.%) alloy exhibited surface slip across both grain and phase boundaries, where the body-centered-cubic (BCC) structure was more resistant to cracking than the orthorhombic (O) Ti2AlNb phase. Overall, surface observations both before and after deformation provided valuable information with respect to the mechanical behavior of the alloys and this will be highlighted in the presentation.

MM9.16
***In − Situ* TEM Study of Self-organization Process of Three-dimensional Nano-void Superlattice in Electron Beam Irradiated CaF_2,.** Tianhua Ding[1], Sha Zhu[1] and Lumin Wang[1,2]; [1]Department of Nuclear Engineering and Radiological Science, University of Michigan, Ann Arbor, Michigan; [2]Department of Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan.

As a widely adopted deep-UV window material and thin film optical coating, CaF_2 may form ordered defect superlattices under electron irradiation. However, the self-organization mechanism of the three-dimensional nano-lattice has not been fully understood and the nature of the defects on the superlattice point (i.e., Ca colloids or voids) has not been certain. In this study, single crystal CaF_2 were irradiated under 200 keV electron beam with in situ TEM observation of the dynamic process of defect ordering. The nano-void superlattice reached steady state after an electron dose of $1\times10^{21} e^-/cm^2$ with void radius about 5 nm and spacing around 20 nm at room temperature. Digital videos recorded during this in-situ observation reveal the dynamic self-organization process of the void superlattice. Coalescence was prevalent at the initial stages. Migration and preferential growth were dominant at the final stages of the superlattice formation. At a dose higher than 3×10^{21} e^-/cm^2 the superlattice structure was destroyed. With the increasing temperature, voids start to become partially faucet at 60°C and the super-structure ordering disappears at 100°C. Small voids coalesce into various sizes in thick area with faceted morphology. The void nature of the defects is confirmed by High-Angle Annual Dark Field image, elemental mapping obtained by Electron Energy Loss Spectroscopy, through

focus imaging and thickness mapping. The void superlattice has simple cubic structure which is parallel to the Fluorine sublattice.

MM9.17
In-situ nano fabrication and electrical characterization for TiO2 nanotubes using dual beam focused ion beam and nanomanipulator. D. K. Cha, J Huang, T Zheng, J.B Jeon, T.H Lee, Jiyoung Kim, R.M Wallace, B.E Gnade and M.J Kim; Electrical Engineering, University of Texas at Dallas, Richardson, Texas.

The one dimensional nano-structures such as carbon and TiO2 nanotubes have unique properties originating from their geometric shapes and quantum size effects. Numerous applications have been suggested in the fields of nanoelectronics, nano-sensors and nano-bio engineering. However, direct manipulation and electrical characterization of individual nanotubes is a critical issue. In this study, we use the dual beam column focused ion beam (DB FIB, NanoLab Nova 200, FEI) equipped with nanomanipulator (Zyvex, S100). This system can provide unique capabilities such as nanolithography and specific site nanofabrication which are critical for electrical characterization for nano size device structures and nanotubes. We focus on direct fabrication of nano-scale test device structures and in-situ electrical characterization for stand alone TiO2 nanotubes using DB FIB with nanomanipulator. TiO2 nanotubes were fabricated by atomic layer deposition (ALD) using nanotemplate method. The nanotubes were spun on top of the SiO2 (10nm)/Si substrates. The resistor test structures were fabricated on specific area (both edge sides of the nanotube) using selective platinum deposition of FIB. The in-situ electrical characterization was performed by nanomanipulator system with nano-probe tips. We present the electrical properties of single TiO2 nanotubes by direct probing on the tubes after positioning them to in-situ generated test patterns using nanomanipulators, and material characteristics of selective deposited test structure using EDS.

MM9.18
SEM-Based Electronic Transport Measurements of Carbon Nanotube Composites and Nanowire Sensors. Stephen Jesse[1], Andrei Kolmakov[2], Yigal Lilach[3], Sergei V. Kalinin[1], Arthur P. Baddorf[1] and David B. Geohegan[1]; [1]Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; [2]Department of Physics, Southern Illinois University at Carbondale, Carbondale, Illinois; [3]Pacific Northwest National Laboratory, Richland, Washington.

Scanning Electron Microscope (SEM) based electronic transport imaging techniques have been used and enhanced in order to view current flow and electronic potential distribution in low-dimensional nanomaterial systems. The two primary imaging modes - electron beam induced current (nano-EBIC) and voltage contrast imaging are introduced and compared with macroscopic analogs and SPM techniques. Compared to conventional EBIC, nano-EBIC achieves resolution of the order of tens of nanometers. This relatively high resolution is due primarily to the fact that the volumes for primary electron collection and secondary electron generation are limited by the dimensions of the thin film or nanowire instead of by beam-sample interaction mechanisms. Additionally, high local curvature enhances local electric fields, substantially enhancing the sensitivity of voltage contrast measurements to variations in surface potential. These imaging modes are demonstrated on single-walled carbon nanotubes (SWNTs) embedded within thin polymer films. Experiments indicate that high contrast, high-definition SEM images of embedded SWNTs within polymers result from highly-localized enhancement of their secondary electron emission resulting from the applied bias and induced electric fields. This new 'electric field-induced contrast imaging' technique, along with specimen current imaging, are applied to determine conducting pathways formed by the nanotubes, and represent general techniques to study electrical transport percolation networks formed by nanorods or nanowires in various matrices. We have also applied these techniques to current nanowire sensors comprised of various materials and subjected to various surface treatments to reveal and measure conducting pathways. Extensions of these techniques to DC and AC modes are discussed. The analytical models for increased current and voltage contrast are discussed. Research was sponsored by the U.S. Department of Energy, under contract DE-AC05-00OR22725 with UT-Battelle, LLC.

MM9.19
Nanomechanics of Biopolymers Studied by In-situ Nanoindentation. Jing Zhou[1], Andrew M. Minor[2], Eric A. Stach[3] and Kyriakos Komvopoulos[1]; [1]Mechanical Engineering, UC Berkeley, Berkeley, California; [2]National Center for Electron Microscopy, Lawrence Berkeley National Laboratory, Berkeley, California; [3]School of Materials Engineering, Purdue University, West Lafayette, Indiana.

There are increasing uses of polymer materials as structural materials in tissue engineering, i.e., cartilage replacement in the artificial human joints, polymeric microtubes for replacement of damaged blood vessels, due to their similarity and compatibility with biological environment. These polymers play significant roles involving various mechanical issues when implanted in human body. For instance, joint replacements need to support body weight while exhibits ultra-low intrinsic friction at the joint interface. Mechanical robustness is required to sustain inner pressure when the polymeric materials were used in circulatory system. So the structural design of biopolymer materials is always closely related to their mechanical responses, which consequently ask for better understanding of the correlation between the mechanical properties and the nanoscale structural evolution of biopolymers. Metal thin films have been studied by in-situ nanoindentation in transmission electron microscopes (TEM), which directly reveals domain and dislocation evolution under applied mechanical forces. Due to the difficulty of fabricating ultrathin freestanding polymer film, in-situ observation of the polymeric objects, especially biomedically interesting polymers, has not been realized. X-ray microdiffraction study shows the change of chain orientation in crystalline region under indentation loading. However, no direct evidence shows how the microstructure of the polymer evolutes in real time and real space. To address this issue, we developed focused ion beam nanomachining approach to fabricate ultra high molecular weight polyethylene (UHMWPE) thin film with controllable thickness around 100nm. The deformation and breakage process of polymer thin film under indentation were imaged through the in-situ characterization in a TEM.

MM9.20
In-situ HRTEM study on surface reconstruction of Bi nanowires. Jinguo Wang[1,2] and Mingliang Tian[1,2]; [1]Materials Research Institute, Penn State University, University Park, Pennsylvania; [2]The Center for Nanoscale Science (MRSEC), Penn State University, University Park, Pennsylvania.

Nanocrystals are of great interest because they exhibit many characteristics which are different from the bulk materials. Bismuth (Bi) is a semimetal with unusual electronic properties that result from its highly anisotropic Fermi surface, low carrier concentration, small effective mass, and long mean free path of the carriers. Because of these unique features, Bi nanorods (nanowires) have been extensively investigated for quantum transport, finite size effects, and magnetoresistance effects. The insights into surafec defect structures have important implications in the application of nanorods in the molecular device technology. Recent study on the surface reconstruction of gold nanoparticles and nanorods has shown that the gold nanorods exhibit <110> surfaces which is different from the bulk materials. We reported here the in-situ HRTEM observation of the surface reconstruction of Bi nanowires with different microstructures. The TEM observation was conducted in a JEOL 2010F transmission electron microscope equipped with EDX and EELS operating at 200 kV.

MM9.21
Probing Structural Order at Solid-Liquid Interfaces with Transmission Electron Microscopy. Wayne David Kaplan and Yaron Kauffmann; Materials Engineering, Technion, Haifa, Israel.

As microstructural length-scales are reduced, the role of interfaces in determining the properties of materials becomes more dominant. The importance of the correlation between interface structure and chemistry with interface (and bulk) properties is evident in a range of material systems, and is a topic of intense experimental and theoretical work for solid-solid interfaces. While detailed thermodynamic analysis of solid-liquid interfaces is routinely conducted, and many works include ex-situ microstructural investigations, knowledge of the local structure at solid-liquid interfaces is still incomplete. To be more specific, the correlation between the structure of the solid, and the structure in the liquid near the interface, has not been fully addressed. In this presentation, in-situ high resolution transmission electron microscopy (HRTEM) of liquid Al in contact with sapphire (α-Al_2O_3) will be presented. Contrast perturbations in the liquid Al adjacent to the crystalline substrate were determined to be due to ordering of the liquid, via rather detailed multi-slice dynamic electron scattering simulations. The ordering effect was further analyzed by molecular dynamics simulations of liquid Al confined by crystalline substrates. These results are compared with recent HRTEM investigations of equilibrium amorphous films at metal-Al_2O_3 interfaces, where partial ordering of the film plays an important entropic role in reaching stable nanometer-thick films. Finally, the concept of combining a monochromatic field emission gun with an aberration corrected imaging system will be described in light of its potential role in studying ordering and segregation at solid-liquid interfaces.

MM9.22
X-Ray Microanalysis of Fully Wet Samples Using WETSEM^{TM} Technology. Irit Ruach-Nir and Daphna R. Yaniv;

QuantomiX Ltd., Nes-Ziona, Israel.

Characterization of chemical microstructures is one of the most important applications of the scanning electron microscope (SEM) equipped with an energy dispersive x-ray spectrometer (EDS). However, one of the challenges this technique was facing is the ability to apply it to wet samples. Typical examples include creams, solutions, suspensions and other liquid containing samples. In this work we show that the recently developed WETSEM$^{\textcircled{tm}}$ technology (QX capsules), provided the solution and enabled direct observation and chemically analysis of samples in their native wet state. WETSEM$^{\textcircled{tm}}$ uses conventional scanning electron microscopes equipped with a standard EDS detector. The technology was used to study the chemical composition of samples from a variety of fields of use including material science and bio-science. Samples of creams, solutions, and other liquid containing specimens such as suspensions of metal, ceramics and mineral particles were analyzed. When using WETSEM$^{\textcircled{tm}}$ technology (QX capsules), the sample is placed in the sealed specimen capsule, and is isolated from the vacuum by a thin, electron-transparent membrane. A metal grid is mechanically supporting the membrane. The thin membrane is used as a window through which imaging and x-ray analysis is carried out. The contribution of the membrane to the sample EDS spectrum was investigated and shown to be negligible. Since the thickness of the membrane is a few hundreds of nanometers and the x-ray signal comes from a much thicker layer the membrane does not interfere with the EDS measurement and its contribution to the EDS spectrum is manifested only by the carbon peak. The grid consists of 330x330 ?m windows. When an EDS spectra is generated from an area within such window the elemental signature of the grid is negligible. This work shows results that validates these conclusions For identification of particles, X-ray spectroscopy (EDS) was applied to a particle of unknown composition. Selected area microanalysis was also used in order to distinguish between adjacent areas in the sample and evaluate homogeneity.

MM9.23
In-situ Observations of Twin Formation Modes in L10-Ordered Intermetallic MnAl. Cagatay Yanar[2], Eric Stach[3], Velemir Radmilovic[4], William Soffa[5] and Jorg M. K. Wiezorek[1]; [1]MSE, University of Pittsburgh, Pittsburgh, Pennsylvania; [2]Alcoa Technology Center, Alcoa Center, Pennsylvania; [3]Purdue University, West Lafayette, Indiana; [4]NCEM - LBNL, Berkeley, California; [5]MSE, University of Virginia, Charlottesville, Virginia.

The tetragonal L10-ordered phase tau-MnAl can form from the disordered hexagonal epsilon phase at temperatures below about 973K by composition-invariant massive ordering and offers attractive uniaxial hard ferromagnetic properties. The technically relevant properties of the L1o-ordered MnAl alloys depend very strongly on the defect structure and the microstructural scale and morphology established during solid-state transfromation. The final microstructures of the fully L10-transformed polycrystals of the ferromagnetic MnAl typically exhibit a high density of twins and planar faults on various length scales. Here in-situ TEM hot-stage experiments have been performed to elaborate the mechanisms and modes by which these twins form during the ordering transformation from epsilon to tau phase MnAl. Post-mortem studies of partially L10-transformed alloys by conventional and high resolution TEM are combined with the dynamic observations of the twin formation mechanisms to ascertain the crystallographic details of the transformation products. Several twin formation mechanisms have been identified during dynamic in-situ TEM experiments. The results from this experimental study are discussed with respect to twin formation mechanisms reported for other related materials systems, e.g. FCC metals and other L10-phases. Support from the National Science Foundation (DMR-Metals) is gratefully acknowledged.

SESSION MM10: Gas-Solid/Liquid-Solid/Oxidation I
Chair: Renu Sharma
Wednesday Morning, November 30, 2005
Hampton (Sheraton)

8:15 AM *MM10.1
In-situ HREM Observation of High Temperature-Gas Reaction. Takeo Kamino[1], Kotaro Kuroda[2], Hiroyasu Saka[2], Hiroshi Makino[3], Yoshinao Suzuki[3] and Keisuke Kishita[3]; [1]Naka Application Center, Hitachi High-Technologies Corporation, Ibaraki-ken, Japan; [2]Graduate School of Engineering, Nagoya University, Nagoya, Japan; [3]Material Analysis Dept., Toyota Motor Corporation, Toyota, Japan.

A specimen heating holder equipped with a gas injection nozzle has been developed for high resolution electron microscopy (HREM) observation of gas-reacted nano-materials at elevated temperatures. A spirally shaped tungsten wire in the diameter of 25μm is used as the heating element and the specimen is directly mounted on the heating element. The power supply unit with a 6 volts-battery is used for the specimen heating, and the maximum heating temperature of 1773K is available. Gas flow rate is precisely controled outside the specimen holder and the pressure of the specimen area in the range between 10-6Pa and 10-2Pa can be obtained during HREM observation. HREM observation ofthe structural changes of nanometer sized Pt catalysts during oxidation and reduction has been carried out using a high resolution 300kV TEM (H-9500). The specimen chamber of the microscope is evacuated by a high-speed turbo molecular pump (TMP) with the pumping speed of 360l/s and the pressure of the specimen chamber was kept in the range of 10-2Pa without increasing the pressure of the electron gun area for certain time. Structural changes of nanometer sized Pt catalysts during the oxidation in air introduced atmospher to the pressure of 2x10-2Pa and also during the reduction of the in situ oxidized Pt catalysts at the pressure of 8x10-6Pa were dynamicaly observed at atomic resolution.

8:45 AM *MM10.2
Dynamic Evolution of Metal/Alumina Interfaces by In situ Heating TEM. Sang Ho Oh[1], Yaron Kauffmann[2], Christina Scheu[1,3], Wayne D. Kaplan[2] and Manfred Ruehle[1]; [1]Max-Planck-Institut fuer Metallforschung, Stuttgart, Germany; [2]Department of Materials Engineering, Technion, Haifa, Israel; [3]Physical Metallurgy & Materials Testing, University of Leoben, Leoben, Austria.

In situ heating transmission electron microscopy (TEM) of thin metal/oxide specimens can provide unique opportunities to study many intriguing aspects in materials science at the atomic length scale: dewetting or wetting behavior of metals on oxides, pre-melting of strained metal surfaces, structural ordering of liquid atoms and dynamic motion of oxide-metal solid-liquid interfaces. We present the experimental results obtained from in situ heating TEM experiments performed with cross-sectional TEM specimens of epitaxial Cu/α-Al_2O_3 interfaces in high resolution TEM (HRTEM) condition. The in situ heating TEM experiments were performed in the Stuttgart high voltage atomic resolution TEM (JEM-ARM 1250, JEOL) operating at 1.25 MeV. This 0.12 nm-resolution-microscope is equipped with a hot stage and a drift compensator (hardware-based), which enables highly stable working conditions at elevated temperatures up to 1000 ^{o}C, and an electron energy loss spectroscopy (EELS) detector for analytical characterization. Thin wedge-shaped Cu (110) foils showed a discontinuous dewetting behavior under the compressive strain ($\sim$7%) which is imposed by α-Al_2O_3 substrate; From the wedge tip, continuous layer-by-layer dewetting occurs by developing the facets parallel to the Cu {111} planes. As the thickness of Cu (110) foil decreases by surface diffusion and when it reaches a certain critical thickness, the crystalline Cu lattice is suddenly disordered and simultaneously shrinks rapidly to the thicker part. During the fast movement thin Cu (110) foil undergoes a complete melting. The observed behavior is analogous to the strain induced pre-wetting transition predicted to occur in thin fcc (110) surfaces under high compressions. The electron beam damage processes occurring in alumina during in situ heating TEM induce the appearance of metallic Al in various forms. Above the T_m ($\sim$660 ^{o}C) of Al, the unoxidized Al atoms rapidly diffuse to the free surface and form liquid Al droplets on the alumina specimen. In thin damaged edges, nucleated liquid Al makes a free standing drop-wise contact with alumina nano-whiskers. Crystal growth of the alumina into the liquid Al, facilitated by interfacial transport of oxygen from the microscope column, was studied in situ at the atomic length scale. In addition, interesting contrast perturbations were observed in the liquid at the interface with the crystal, probably caused by structural ordering of the liquid atoms imposed by periodic interactions with the crystal.

9:15 AM *MM10.3
In situ observations of catalyzed crystal growth.
Frances M. Ross, S. Kodambaka, J. B. Hannon, R. M. Tromp, J. Tersoff and M. C. Reuter; IBM Research Center, Yorktown Heights, New York.

By using small catalyst particles to enhance crystal growth in specific locations, it is possible to grow crystalline material in the forms of wires, ribbons or tubes. Such structures may be used as frameworks for three dimensional electronic devices, and have also been suggested for applications such as interconnects, logic elements and photonic bandgap crystals. As with any self-assembly process, understanding the growth mode in detail should help us to optimize the structures produced. We have therefore examined catalyzed crystal growth in situ, recording videos in an ultrahigh vacuum electron microscope which has gas handling capabilities so that growth can be carried out during observation. The materials system we have studied is the vapour-liquid-solid growth of silicon and germanium nanowires using gold as the catalyst. In this talk we will discuss some of the

experimental issues associated with making quantitative observations of catalyzed crystal growth and will then describe measurements of wire growth kinetics, focusing in particular on the role of catalyst diffusion, the effect of reactive species such as oxygen, and the structure of the catalyst. These observations allow us to understand some of the constraints on catalyzed crystal growth and suggest conditions under which uniform wires can be grown for applications.

SESSION MM11: Gas-Solid/Liquid-Solid/Oxidation II
Chair: Takeo Kamino
Wednesday Morning, November 30, 2005
Hampton (Sheraton)

10:15 AM *MM11.1
InSitu **Observations of Growth mechanmisms of Carbon Nanotubes using Environmental Transmission Electron Microscope.** Renu Sharma, Arizona State University, Tempe, Arizona.

Carbon nanotubes have attracted much attention since their discovery because of their remarkable properties. However, the selective synthesis of nanotubes with a desired structure and property is still a challenge. Moreover, for some applications, such as field emitters, they need to be synthesized directly as part of the device or the circuit. In order to determine the best synthesis conditions for a certain type of CNT, it is important to understand the relationship between the synthesis conditions (temperature and pressure) and their structure and properties. We have employed *insitu*TEM observations of the nucleation and growth of CNT as they are formed to understand their formation mechanism. We have used a specially modified environmental transmission electron microscope (ETEM), a Tecnai F20, operated at 200KV and equipped with a Gatan imaging filter (GIF) and annular dark-field detector for dynamic observations. Ni/SiO_2 catalyst samples were dry loaded on Ni grids and heated up to 400-700^{o}C in the microscope vacuum (10^{-6} Torr) using a furnace-heating holder. 10-100 mTorr of acetylene (C_2H_2) was slowly leaked into the sample region at the reaction temperature, and bright-field images were recorded using a digital video recorder connected to a TV rate camera. The growth rates and growth mechanisms were obtained by studying sequential video frames. CNT growth profiles under different reaction condition were generated and the incremental change in projected length during each frame (1/30 sec) was used to estimate instantaneous growth rates for each frame. The growth rates measured in this manner were broadly distributed, and indicative of discontinuous growth. Our data show that the growth rates, duration of growth, structure and length of the CNTs formed, are controlled by the synthesis conditions. For example, total growth time of individual CNTs after nucleation was observed to be longer at lower gas pressures (15-45 sec compared to 3-5 sec at high gas pressures). At gas pressures above 20 mTorr, nanotubes grew up to 340 nm in length, in a serpentine manner while straight single wall carbon nanotubes grew at low pressures ($\sim$10 mTorr) with an average length of $\sim$50 nm. Thus we have been able to obtain a better understanding of the relationship between synthesis conditions and CNT nucleation and growth mechanism that will be discussed in detail.

10:45 AM *MM11.2
The Surface Dynamics of Cu and Cu-Au Oxidation.
Judith C. Yang, Materials Science and Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania.

Fundamental understanding of oxidation is important for corrosion, catalysis, as well as oxide thin film processing. As our devices approach the nanoscale, understanding their environmental stability at this length scale will be critical to their performance. Yet, these initial oxidation stages, from nucleation to coalescence of an oxide scale, is still surprisingly a terra incognita. In situ ultra-high vacuum transmission electron microscopy (UHV-TEM), is ideal for visualizing these initial oxidation stages since the structural changes can be seen in real-time under well-controlled surface conditions. The dynamic responses of Cu and Cu-Au thin films to variations in thermodynamic variables such as temperature, oxygen pressure, strain, and crystallographic orientation, were monitored. The nucleation and growth behavior of three-dimensional oxide islands demonstrate that oxygen surface diffusion is the rate-limiting mechanism for oxide formation during initial oxidation, thereby demonstrating a greater universality of heteroepitaxial concepts. Models based on surface orientation, strain development, and diffusion will be discussed to explain the formation of some of the novel oxide nano-structures.

11:15 AM MM11.3
The High Temperature Initial Oxidation Stages of CuAu(100) Investigated by *Insitu* **UHV-TEM.** Li Sun and Judith C. Yang; Department of Materials Science and Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania.

For alloy oxidation, most traditional methods focus on the analysis of post-oxidation structures which cannot provide real time information about nucleation and initial growth of oxide. However, *insitu* UHV-TEM (ultra high vacuum-transmission electron microscopy) experiments can provide visual oxidation processes in real time and dynamic information of oxide islands at the nanometer scale. This experimental tool provides unique and critical data of these gas surface reactions in a wide pressure and temperature range needed for a fundamental understanding of the atomistic kinetics. Our previous studies by *insitu* UHV-TEM using Cu as a model system have successfully demonstrated that heteroepitaxial concepts describe the nano-oxidation of metals. Recently, we have extended our studies to binary alloys, specifically CuAu, because Au does not form stable oxide and is miscible to Cu at our experimental conditions and compositions, so that the results can be readily compared with Cu nano-oxidation. Here, we mainly focus on the initial stage of oxidation of $Cu_{0.5}Au_{0.5}$(100) from 800 ^{o}C to 1000 ^{o}C in order to extend our earlier studies, which center on $Cu_{0.5}Au_{0.5}$(100) oxidation mechanisms that occur at temperatures from 550^{o}C to 750^{o}C [1]. For the lower temperature range (550^{o}C-750^{o}C), double pyramid Cu_2O islands form with cube-on-cube crystallographic orientation with respect to the film, Compared with Cu(100) nano-oxidation, $Cu_{0.5}Au_{0.5}$ alloy has much slower kinetics toward oxidation and longer incubation time at the same temperature. Oxides in $Cu_{0.5}Au_{0.5}$(100) grow with sub-linear power law dependence which is due to the build-up of Au atoms near the reaction front. In this study, the higher temperature range (800^{o}C- 1000^{o}C) $Cu_{0.5}Au_{0.5}$(100) oxidation will be examined, and the similarities and differences between the results at higher temperature range and at lower temperature range will be compared to see if the same model is applicable. [1] L. Wang, J.C. Yang,"The reduced copper oxidation kinetics due to Au alloying in $Cu_{0.5}Au_{0.5}$(001) investigated by *insitu* UHV-TEM", Journal of Materials Research, *Insitu* TEM focus issue, has been accepted.

11:30 AM *MM11.4
The Role of *InSitu* **Electron Microscopy in the Design of Nanomaterials for Environmental Catalysis and Alternative Energy Sources.** Pratibha Gai, Central Research & Development, DuPont, Wilmington, Delaware.

Global challenges of the 21^{st} century include, maintaining clean environment, sustainable alternative energy sources and novel green routes to polymers. Today, our world faces a variety of challenges in creating alternative energy sources, reducing global warming and environmental impact from industrial processes. The development of advanced methods in the design of molecular and nanostructural systems in catalysis are needed to meet these challenges. *Insitu* atomic resolution-environmental electron microscopy (ETEM) is a powerful method in understanding and predicting how dynamic catalysts work at the atomic level. In this presentation, I will describe the first *insitu* atomic resolution environmental-TEM (ETEM) developed in our laboratory to study dynamic gas adsorption on the surface of nanocatalysts and carbon nanostructures to engineer nanomaterials to meet these demands. The ETEM is capable of atomic resolution under gas pressures of a few mbar and temperatures up to 1000°C and gas-solid reactions can be monitored as they take place. Probing reactions in wet environments at the nanoscale is also possible. Most recently, our research is focused on the development of nanostructures for emission and pollution control and heterogeneous hydrogenation routes using nanoparticles on nanosupports which exhibit unique chemical reactivity in clean polymer technology. In addition, we have investigated nanomaterial architectures based on doped-carbon nanotubes and related nanostructures as candidates for energy storage. The results exemplify the pivotal role of advanced *insitu* electron microscopy methods in the design of nanostructures for environmental catalysis, polymer technology and alternative energy sources.

SESSION MM12: Irradiation
Chair: Ian Robertson
Wednesday Afternoon, November 30, 2005
Hampton (Sheraton)

1:30 PM MM12.1
Dose-dependent EELS of spinel MgAl2O4. Nan Jiang, Physics, Arizona State University, Tempe, Arizona.

Spinel MgAl2O4 has potential applications in fusion energy systems due to its radiation resistance.Under high-energy (1MeV) electron irradiation, the MgAl2O4 underwent a progressive phase transformation along with the gradual decrease of Mg in between 750 and 850C, and did not produce any dislocation type damage. On the contrary, dislocation loops were formed by 1MeV electron irradiation,

followed by precipitation of metallic Mg in the range 900 to 1130K. It is also reported that electron irradiation induces cation disordering between the tetrahedral and octahedral sites at 870K, and slight evacuation of cations from the tetrahedral to octahedral sites also occurs. These confusions can be at least partly on account of the variety of irradiation conditions. Whether a mater is radiation resistant also depends on the sensitivity of the technique to evaluate the degree of damage. Unfortunately, the most previous studies relied on TEM images to identify dislocation loops, voids, and defect clusters, which are in fact the accumulation of damage. Such post-radiation observations might not be able to reveal the initial process of radiation damage, and cause the confusion on the fundamental role of radiation in MgAl2O4. Therefore, it is absolute important to be able to observe the initial atom migrations induced by irradiation in situ. Here we combine electron irradiation with EELS technique, called dose-dependent EELS (DDEELS), to directly observe the atom migrations in MgAl2O4 under irradiation. In this method, the irradiation process is controlled by incident electron flux, and the irradiation effects can be monitored by EELS in real time. The basic idea of DDEELS is as follows. Providing that the Mg and Al migrate between tetrahedral and octahedral interstices under electron irradiation, the EELS of Mg and Al core edges should show the changes, which can be directly related to the initial process of electron irradiation in MgAl2O4. In short, we found that under electron irradiation Mg move gradually to the octahedral interstices. On contrast, Al do not fill back in the tetrahedral interstices, but rather redistribute within the octahedral interstices. Driven Mg into octahedral interstices by electron irradiation can be qualitatively explained as follows. Electronic excitation by fast electrons causes that some electrons in atoms are driven out of the trajectory of the beam. The trajectory region thus becomes charged positively providing charge neutrality cannot be immediately restored from surroundings. Due to the difference in formal valence states, an Mg on an Al site in octahedron bears a negative charge, while an Al on an Mg in tetrahedron bears a positive charge. Under positive electrostatic field, Mg in octahedron becomes stable, while Al in tetrahedron becomes unstable. As a result, both Mg and Al have tendency to occupy octahedral interstices. This work is supported by NSF Grant DMR0245702.

1:45 PM MM12.2
Self-Annealing of Fast Electron Damage in a Glass.
Andre Mkhoyan and John Silcox; Applied Physics, Cornell University, Ithaca, New York.

Silicate based compositions and, in particular, aluminosilicates are the most common and widely studied among the glass composites. It is well known that such silicate glasses can be easily damaged under irradiation by ion beams or electron beams, or even by lasers and UV beams. The conventional view of the damage in silicate glasses is that it is irreversible. Such a view made intentional damage of the silicate glasses an alternative method for modification of the original network to achieve new electrical, optical and structural properties. Here we report the surprising observation of reversal of the damage in aluminosilicates ((CaO-Al2O3)0.9(2SiO2)0.1) glass and full self-recovery even after intense (but limited) electron-induced damage at room temperature. Here we provide an understanding of what are the underlying atomic mechanisms and how they play out in the damage and possible recovery mechanisms by the use of scanning transmission electron microscopy (STEM) both to damage and to observe in situ recovery of the sample. We also used electron energy loss spectroscopy (EELS) to monitor changes in the chemistry on the atomic scale. During exposure of the area changes in the chemical composition of the glass were studied by simultaneously recording ADF images and core-level EELS spectra of the components: O K-edge, Ca L2,3-, and Al L2,3 and Si L2,3-edges. After intentionally damaging the glass for a short period of time, the beam was deflected away from the damaged area. The recovery process was studied by periodically recording ADF images of the damaged area. At the end, when the glass was fully recovered, the EELS spectra of the same components from exactly the same area were measured again. The results of our EELS data analysis based on measuring the fine structure of the core-level EELS of glass components and recording compositional sensitive ADF-STEM images clearly indicate that despite massive mass-loss by driving Ca atoms away from the damaged area and significant phase-transformations during the electron beam damage, CaO-Al2O3-SiO2 glass can recover from the damage in both the composition and in structure making recovery complete. To explain why such recovery has not been observed previously in other electron-beam-induced damage experiments on similar CaO-Al2O3-SiO2 glasses, we also conducted experiments on glasses with different compositions. Results indicate that concentration of SiO2, provider of network forming element SiO4, is critical for a degree of reversibility of the damage; as higher concentration of the SiO2 in glass the lower is the reversibility.

2:00 PM MM12.3
An In-Situ TEM Study of Carbon Aerogels and Their Metal-Loaded Analogs. Dafei Kang[1], Can Erkey[2] and Mark Aindow[1]; [1]Materials Science and Engineering, University of Connecticut, Storrs, Connecticut; [2]Chemical Engineering, University of Connecticut, Storrs, Connecticut.

Carbon aerogels (CAs) represent a new class of mesoporous materials that are characterized by uniform pore sizes, low bulk densities, very high surface areas and high electrical conductivities. These properties make them attractive for applications such as the electrodes in supercapacitors and fuel cells, and as the support for catalytic nanoparticles. The synthesis of pure CAs follows a sol-gel route first established by Pekala et. al. The pore properties of CAs were tailored by carefully controlling the key parameters of the synthetic reaction from which the CA is derived. Precious metal (e.g., Pt and Ru) with catalytic activities were incorporated into the CA matrix as highly-dispersed nanoparticles with narrow particle size distributions via a novel supercritical fluid deposition method. The structural and chemical characterization of both pure and metal-loaded carbon aerogels were conducted using a Jeol 2010 FasTEM high-resolution TEM operating at 200kV. The basic structure of both naked CAs and their metal-loaded analogs remained stable at the normal imaging current densities of the TEM used. In an extended study presented here, the pure CAs and their metal-loaded analogs were exposed in-situ to enhanced electron irradiation in the TEM column, which was controlled by adjusting the condenser aperture size and magnification of the TEM. It was found that the characteristic tortuous structure of CAs of various densities (ranging from 0.26 to 1.40 g/ml) underwent significant re-organization and multi-shelled onion-like structures developed. Similar structures were also observed for metal (Pt, Ru)-loaded CAs although the rate of such transformation appeared impaired slightly by the presence of heavy metal particles. This in-situ behavior of CAs in TEM provides some interesting new information about the phase stability of disorderded carbons under off-equilibrium conditions.

2:15 PM MM12.4
Microstructure Evolution of the Au-Si Nanowire Junction Under the Electron Beam Irradiation in Transmission Electron Microscope. Quan Li, Physics, The Chinese University of Hong Kong, Hong Kong, Hong Kong.

A special type of Au-Si nanowire heterojunction, which is wrapped by SiO2 surface layer, has been synthesized using thermal chemistry method. Transmission electron microscopy study of the nanowire junction reveals the existence of nanochannel in-between the Si core and SiO2 sheath close to the junction, providing a reversible flowing path for the Au under the continuous electron beam irradiation in the microscope. The Au-Si interactions during the flowing process lead to an interesting phase evolution of the junction system, which eventually result in self-formation of the secondary nanostructures at the original Si/SiO2 interface. The observed microstructure/phase evolution of the Au-Si nanowire junction under the focused electron beam irradiation suggests a novel approach to modify and pattern the Si nanowire surface, which may have potential applications in the nanoelectronic industry.

SESSION MM13: Microstructure/Instrument Development
Chair: Eric Stach
Wednesday Afternoon, November 30, 2005
Hampton (Sheraton)

3:30 PM MM13.1
View and Work in Microscopy: Latest in Stages and Substages Development. Walter Kammrath, Administration, Kammrath & Weiss, Dortmund, NRW, Germany.

The microscope should not just view, or take a chemical analysis, but its capabilities should be enhanced by actually performing simple ore even complex activities. Several examples of stages, and substages for in-situ thermal, micro mechanics and micro electronics experiments are shown in this presentation. These devices were designed to perform many operations known from macroscopic procedures, under the viewing microscope beam. The accent is set on the term modular, where a simple starting configuration can be upgraded or supplemented by add-ons to grow into testing and manipulating instruments for scientific in-situ studies. As a typical example for this, a family of testing substages for materials testing (tensile, compression, bending, etc.) is shown, all of which will run with the same drive electronics. Some test procedures will not allow more than a single cycle for each individual specimen, therefore another guiding design feature is, to take these instruments from one microscope to the other (such as from the SEM to a FIB, an AFM, ultrasonic, or

light microscope) during a single load test, without having to take out or relax the specimens. Some of these substages are placed on top of the specimen stage while the chamber vented, others have to be incorporated by an airlock interchanger. A brief example is shown, covering the development from the first sketch to a serial product. Comments about the degree of complexity in the micron and nanometer precision class will round up the presentation.

3:45 PM MM13.2
A versatile three-contact electrical biasing transmission electron microscope specimen holder for electron holography and electron tomography of working devices.
Rafal Dunin-Borkowski[1,2], Takeshi Kasama[2,1], Alan Robins[3], David Smith[3], Jeff Gronsky[3], Christine Thomas[3] and Paul Fischione[3]; [1]Department of Materials Science and Metallurgy, University of Cambridge, Cambridge, United Kingdom; [2]RIKEN, Wako, Saitama, Japan; [3]E.A. Fischione Instruments, Inc., Export, Pennsylvania.

The concept of a 'laboratory in an electron microscope', which allows several high spatial resolution analytical techniques to be combined with experiments that are traditionally carried out ex situ, is highly attractive for tackling a wide range of problems in nanoscience and nanotechnology. We have recently developed a novel transmission electron microscope specimen holder that allows a sample to be examined under an applied bias using both electron holography and electron tomography, as well as allowing the same sample to be transferred easily to a scanning electron microscope, a focused ion beam workstation, a plasma cleaner and an argon ion miller in a universal cartridge assembly. Within the cartridge, two independent electrical contacts can be made to the surface of the specimen. When the cartridge is located in the specimen holder, a third electrical contact (typically an etched tungsten needle) can be moved towards the specimen using piezoelectric drives. Tilts of up to 70 degrees can be achieved before the central 0.5 mm of the sample begins to be shadowed by the edges of the holder. Here, we demonstrate recent results from the use of this specimen holder to characterize electrostatic and magnetic fields in working devices, including field emitters and electrical circuits patterned onto electron-transparent films, using off-axis electron holography. We also demonstrate the use of the holder to perform nanoindentation experiments, and the design of an alternative cartridge geometry that allows samples to be heated to 1500 degrees C during examination in the electron microscope.

4:00 PM MM13.3
Directly observing the kinetic pathways that evolve the microstructure and morphology of hetero-epitaxial films.
Kevin F. McCarty[1], Winnie L. Ling[1], Konrad Thuermer[1], Norm C. Bartelt[1] and C. Barry Carter[2]; [1]Sandia National Laboratories, Livermore, California; [2]University of Minnesota, Minneapolis, Minnesota.

Hetero-epitaxial films frequently contain microstructural defects and have surface morphologies that complexly evolve during film growth and annealing. With time, for example, microstructural defects such as twin boundaries can be introduced or eliminated and the surface morphology can become either smoother or rougher. Given the large number of possibilities, knowing what kinetic pathways actually evolve microstructure and morphology can be challenging. In this work, we use low-energy electron microscopy (LEEM) to directly identify some of these kinetic pathways. As a model microstructural defect, we study crystallographic twins in Ag films. We directly observe that Ag islands nucleate with two different stacking sequences on a Ru(0001) substrate. Where differently stacked islands impinge, a twin boundary occurs. Individual twin boundaries were tracked with LEEM during growth and annealing. Surprisingly, the twin boundaries move readily during film growth but relatively little during annealing. The growth-driven motion of twin boundaries occurs as film steps advance across the surface – as a new atomic Ag layer approaches an twin boundary, the advancing step edge carries along the boundary. This coupling of the microstructural defect (twin) and the surface step during growth can produce large film regions that are twin free. A second unexpected kinetic pathway is the role of atomic substrate steps in film de-wetting. At equilibrium films often do not uniformly wet their substrates. Instead, three-dimensional (3-D) islands form to lower free energy, exposing the bare substrate or a very thin wetting layer. This de-wetting requires diffusion from the thinner to the thicker film regions and involves the rearrangement of surface atomic steps. Because of the energetic cost of creating steps, a large free-energy barrier restricts thickening of any island by new-layer nucleation. How 3-D islands avoid this barrier and thicken during de-wetting has not been generally explained. We have used to ability of LEEM to image in real-time the motion of surface steps and determine the local film thickness to solve this puzzle. We show that the coinage metals (Cu, Ag, and Au) grown on Ru(0001) and W(110) substrates only de-wet in the presence of substrate steps, through a remarkable nucleation-free process that involves islands migrating in the downhill direction of the substrate, thereby increasing their average thickness. Without substrate steps, 3-D islands form neither during growth nor upon annealing. This research was supported by the Office of Basic Energy Sciences, Division of Material Sciences, U.S. Department of Energy, under Contract No. DE-AC04-94AL85000.

4:15 PM MM13.4
In-situ Microscopic Study of Cu Intragranular Electromigration. Kuan-chia Chen, Chien-Neng Liao, Wen-Wei Wu and Lih-Juann Chen; Materials Science & Engineering, National Tsing-Hua University, Hsinchu, Taiwan.

Electromigration (EM) in unpassivated copper lines at room temperature is investigated in ultra-high vacuum by in-situ transmission electron microscopy (TEM). The electric current induced atomic migration in a (211)-oriented Cu grain has been successfully recorded in real-time video. The atomic image inside the (211) grain was found to vanish directionally when applying an electric current density of 2×10^6 A/cm^2 through the Cu line. The preliminary results suggested the combination of {111} planes and <110> directions to be the easiest EM path in crystalline copper. By performing selective area diffraction (SAD) analysis on a singular Cu grain with (111) crystal orientation, some unusual electron diffraction patterns were recorded after passing an electric current through the Cu line for a short period of time. It is believed that the EM-induced short-range-ordered vacancies may be held responsible for the additional diffraction patterns. Finally, the dependence of crystal orientation on EM-induced atomic migration behavior and microstructure evolution will be discussed.

4:30 PM MM13.5
Quantitative Kinetic Analysis of Thin Film NiTi Crystallization using in situ TEM. Hoo-Jeong Lee, David T. Wu, Hai Ni and Ainissa G. Ramirez; Mechanical Engineering, Yale University, New Haven, Connecticut.

The crystallization of amorphous NiTi thin films was studied using in situ transmission electron microscopy (TEM) methods. Samples were subjected to heating conditions within the microscope and the microstructural development was monitored and recorded. The nucleation rate and the growth rate were determined experimentally by noting the number of new grains per frame and their change in size. These parameters were compared to the conventional method of kinetic analysis using the Johnson-Mehl-Avrami-Kolmogorov (JMAK) theory and found to have reasonable agreement. A consequence of this experimentally-determined description of nucleation and growth is the ability to predict the average grain size over a broad range of temperatures. This quantitative analysis derived from in situ studies provides the groundwork for the control of microstructures and properties in NiTi shape memory alloy thin films.