SYMPOSIUM P
Electron Microscopy of Molecular and Atom-Scale Mechanical Behavior, Chemistry, and Structure

November 29 - December 1, 2004

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* Invited paper
We have demonstrated the first images with statistically significant contrast from individual impurities inside a crystalline host using Z-contrast STEM [1]. These images of single Si atoms in Si revealed that the contrast from these impurities allowed for rendering these dopants electically inactive must contain two Si atoms. The details of the Si atom image intensity depend strongly on channeling of the electron probe onto the atomic columns of the zone-axis crystal. The probe localization due to channeling enabled us to measure sub-Angstrom off-substitutional displacements of the Si atoms, leading to a new intrinsic defect structure in heavy doped Si [2]. Despite these successes, our efforts were hampered by the need for exceptionally thin samples (< 5 nm) and the lack of information about the depth of the atoms in the sample. Spherical aberration corrected STEM promises to mitigate these difficulties. Using a smaller probe increases the signal from substitutional impurities, allowing thicker samples, and the increased numerical aperture may be enable useful 3D imaging by optical sectioning. The current generation of corrected STEM [3] has a calculated resolution along the optic axis of 6.4 nm; future instruments will be better. However, simulations indicate that probe channeling may dominate optical defect in zone-axis crystals, complicating interpretation of these images. [1] P. M. Voyles et al., Nature 416, 826 (2002). [2] P. M. Voyles et al., Phys. Rev. Lett. 91, 125505 (2003). [3] Mc. 50, 177 (2001). PMV acknowledges support from the UW NSF MRSEC on Nanosstructured Materials and Interfaces (NSF DMR-0076983).

Imaging Single Atoms with Z-contrast STEM: Current Results and Future Prospects, Paul Voyles, David A. Muller and John Gruner.

Aberration-corrected Z-contrast (HAADF) STEM offers significant advantages for materials research due to its superior resolution and sensitivity, which allows observation of atomic-scale phenomena with unprecedented detail. ORNL’s 300 keV VG Microscopes HB603U STEM with Nion aberration corrector has a demonstrated resolution of 0.61 Angstroms and routinely allows imaging of single atoms inside materials. These levels of performance not only provide a direct link to first-principles calculations by facilitating the solution of complex materials problems, but in particular, aberration corrected STEM is a powerful tool for the study of dopant structure simultaneously, providing more details on their electronic structure as well as the segregation behavior at the interfaces. Aberration-corrected scanning transmission electron microscopy (STEM) is an ideal tool to study the atomic and electronic structure as well as the segregation behavior at semiconductor hetero-structures with unprecedented detail and a lateral resolution of 0.61 Angstroms has recently been achieved. To gain 3D information about the single HF atom distribution at the Si/SiO2/HfO2 interface a through-focus series technique was applied, enabling high-angle annular dark-field images in the cold-field emission mode of the STEM. The usage of rather large convergence angles (20 to 30 mrad) provides a limited depth of focus, and, therefore, a spatial resolution of around 1-3 nm parallel to the optical axis. Additional 3D reconstruction techniques, such as conventional tomography, were hampered by the need for exceptionally thin samples (≤ 5 nm) and the lack of information about the depth of the atoms in the sample. Spherical aberration corrected STEM promises to mitigate these difficulties. Using a smaller probe increases the signal from substitutional impurities, allowing thicker samples, and the increased numerical aperture may enable useful 3D imaging by optical sectioning. The current generation of corrected STEM [3] has a calculated resolution along the optic axis of 6.4 nm; future instruments will be better. However, simulations indicate that probe channeling may dominate optical defect in zone-axis crystals, complicating interpretation of these images. [1] P. M. Voyles et al., Nature 416, 826 (2002). [2] P. M. Voyles et al., Phys. Rev. Lett. 91, 125505 (2003). [3] Mc. 50, 177 (2001). PMV acknowledges support from the UW NSF MRSEC on Nanosstructured Materials and Interfaces (NSF DMR-0076983).
for scanning transmission electron microscopy (STEM) now offers the structural changes in Ti-O octahedra and resulting grain boundary structure and composition occurring at the dislocation core. The study of the SrTiO₃ model system. This study uses an undoped 4° such as ferro-electricity, mixed conductivity, and high- Tc of Perovskite Oxide Systems by Atomic Resolution Electron atomic resolution scanning transmission electron microscopy and microscopie electrical transport measurements.

Measuring the Interfacial Potential in Thin Grain Boundaries of Perovskite Oxide Systems by Atomic Resolution Electron Energy-Loss Spectroscopy, Robert Friedrich Klie and Yimei Zhu; Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York. Polycrystalline perovskite-oxides exhibit a wide variety of properties, such as ferro-electricity, mixed conductivity, and high-Tc superconductivity. Many of these properties are heavily influenced by the presence and behavior of grain boundaries. Current theories introduce generic grain boundary states to explain the microscopic properties of grain boundaries that lead to the formation of a double Schottky barrier. In these models, the boundary states are induced by the presence of a 2-D sheet of immobile charges in the grain boundary plane, which are compensated by an opposite space charge in a depletion layer on either side of the boundary. While this model assumes a homogeneous distribution of these grain boundary states, which is strictly only true for high-angle interfaces where the grain boundary dislocation core overlap, it cannot account for local variations in the density of grain boundary states. In addition, this model assumes that in the area close to the dislocation cores, all charge carriers are completely depleted up to the width of the depletion layer. The Schottky model is therefore unsuitable for low-angle interfaces in materials with a screening length of less than 4 nm. Aberration correction enables smaller, brighter probes with resulting high resolution energy loss spectroscopy (EELS) images and will be used to demonstrate how the defocus configurations affect both types of images and will be used to probe the possibility of quantifying oxygen content in the vicinity of defects in ceramic materials.

Advanced Transmission Electron Microscopy Studies of the LaAlO₃/Si Interface, Dimitri G. Kleman¹, Daniel Schlenoff², L. Hsu³ and Susanne Stemmer³; ¹Materials, University of California, Santa Barbara, California; ²Materials Science and Engineering, Penn State University, University Park, Pennsylvania; ³Microelectronics and Physical Sciences Laboratory, Motorola, Tempe, Arizona.

The performance of novel field-effect transistors that employ epitaxial oxides as gate dielectrics is determined by the atomic structure of the interface between the oxide and Si. Oxides with the perovskite structure are attractive gate dielectrics, because among those oxides that are thermodynamically stable in contact with Si, perovskite have the highest k values. The SrTiO₃/Si interface has been extensively characterized. The perovskite LaAlO₃ is attractive because it has a dielectric constant of 24, a bandgap of 5.6 eV, large band offsets with Si and a relatively small lattice mismatch with Si (1.3 %). In contrast to (001) SrTiO₃, stoichiometric (001) LaAlO₃ surfaces are polar and exhibit long range ionic order. However, strong state charge of -1 on La and +1 on O, respectively. SrTiO₃/Si and LaAlO₃/Si interfaces are thus expected to be fundamentally different. To obtain direct interfaces that allow for a fundamental understanding on the LaAlO₃/Si interface, Si was grown epitaxially on (001) LaAlO₃ single crystals by molecular beam epitaxy (MBE). In conventional high-resolution transmission electron microscopy weak periodic changes in the image contrast are seen under certain defocus/thickness values along the interface. To interpret the interface contrast, image simulations of different pre-conceived starting models would have to be performed. We have used atomic resolution high-angle annular dark-field imaging in scanning transmission electron microscopy to directly obtain the atomic structure of the epitaxial interface between (001) LaAlO₃ and Si. In these images, an unusual 3x1 interface reconstruction, in which every third La column is removed from the interface plane, is observed. Shifts of the Si lattice by half a unit cell along the interface indicate the existence of a low-energy interfacial configuration. The interface atomic structure is discussed in the context of electronically-favorable interfacial bonding, in which Si dangling bonds and charge built up at the interface between the ionic oxide and Si are avoided, and models that are consistent with the atomic structure of the interface are examined. These results are used to develop a new model of the grain boundary potential in SrTiO₃. This work was supported by the Division of Materials Sciences, U.S. Department of Energy, under Contract No. DE-AC02-08CH10886.

 SESSION P2: Electron Energy Loss Spectroscopy for Sub-nanometer Chemical and Optical Properties
 Chairs: Nigel Browning and Ondrej Krivanek
 Monday Afternoon, November 29, 2004
 Gardner (Sheraton)
 1:30 PM P2.1 High Resolution Energy Loss Spectroscopy in Materials
There is increasing interest in energy loss spectroscopy in the transmission electron microscope using monochromators of the electron source. Such systems are designed to achieve an energy resolution of 0.1-0.2 eV while maintaining a probe size of approximately 1 nm. There are also different approaches to achieving a high energy resolution in energy loss spectra using cold-field electron emissions sources and numerical deconvolution techniques. There is therefore growing interest in understanding the limitations and advantages of the various approaches in real materials science applications. This presentation will discuss the applications of a monochromated system to a range of materials in the low-loss and core-loss regime of the energy loss spectrum to show the potential of high-resolution spectroscopy techniques in materials science. I will also discuss data acquired with a monochromator and a cold-field emission source and compare these results with data processed using numerical deconvolution algorithms available in the open literature. Some of the spectra will be compared with X-ray absorption data.


The recent development of aberration correctors and monochromators for field-emission (scanning) transmission electron microscopy (STEM) has opened up new levels of spatial resolution for both Z-contrast and phase-contrast imaging. An additional benefit for analytical microscopy is the ability to obtain electron energy loss spectra (EELS) with increased spatial (0.01 nm) and energy (0.15eV) resolution. With two different STEM configurations one can permit the optimal spatial resolution to be coupled with the highest energy resolution, for reasons of source demagnification, signal levels, and simply that the complete monochromated- aberration corrected system has not been built yet, the practical limits of spatial and energy resolution still permit detailed spectroscopic analyses to be performed for many materials science applications. Specifically, using a monochromated Schottky field emission FEI Tecnai G2 an energy resolution of 0.15eV can be coupled with a 1nm probe size, using a cold-field emission Nion Cs-corrected VG microscope, a 0.4eV energy resolution can be coupled with a 0.01nm probe size. These two levels of performance are ideally suited to two different types of analyses. The 0.15eV energy resolution and 1nm spatial resolution is useful for the analysis of the low-loss region of the spectrum (lower spatial resolution from delocalization), permitting quantum confinement effects and optical responses of individual nanostructures to be measured. The 0.01nm energy resolution and 0.01nm spatial resolution is useful for the analysis of the core-loss region of the spectrum (high degree of localization but energy broadening due to the lifetime of the final state), permitting spectroscopy to be performed from individual defects. In this presentation the current configurations for high energy/spatial resolution EELS will be discussed with reference to the instrumentation developments needed to further improve performance. Results will be presented from the analysis of individual quantum dots in nanocrystalline polytetrafluoroethylene and carbon nanotubes and individual dislocations and stacking faults in GaN to highlight the advantages of performing EELS with this level of resolution.

EELS Analysis of Interstellar Dust Particles Using a Monochromated Scanning Transmission Electron Microscope, Rolf Ems7, Nigel D. Browning1, Zuxiang R. Dai9 and John P. Bradley3.

Interplanetary dust particles (IDPs) collected in the stratosphere are an important resource of early solar system and presolar interstellar grains. They are heterogeneous aggregates of submicrometer-sized grains that contain amorphous silicates, organic carbon, implanted gases, and a variety of nanometer-sized inclusions including metals, and Fe,Ni sulfides. IDPs are thus unique examples of natural nano-materials of high complexity. The study of the structure and composition of IDPs, e.g. condensation states of inclusions, mass loss of gases in individual pores, and the radiation characteristics requires an experimental technique providing a highly sensitive analytical capability at high spatial resolution. High energy-resolution (low-loss) EELS was carried out using an FEI Tecnai F30 U-T scan transmission electron microscope equipped with a high-resolution EEL spectrometer and a double-focusing Wien filter acting as a monochromator. This electron optical configuration delivers a 1 nm sized electron probe with an energy resolution in EELS of 0.16 eV, enabling local probing of inclusions in various types of IDPs. Gas bubbles in amorphous silica were analyzed by low-loss EELS. Spectral features caused by molecule excitation as the Schumann-Runge and the BANDALO band revealed the presence of O2. Such detailed spectral information is commonly accessed using UV spectroscopy. However, owing to the size of the bubbles (10 nm) and the limited spatial resolution of UV spectroscopy, in the present case, the use of high energy-resolution EELS performed in scanning transmission provides an indispensable way to distinguish the signal stemming from the gas and the silica matrix. The presence of O2 is confirmed by the O K-edge. The pi peak of molecular O2 is clearly distinguishable by width (0.9 eV) and position (535 eV) from the pre-peak observed for other gases (2 eV width at 531.5 eV). The oxidation state of Fe (6.2±0.7) in Fe-oxide particles measured by the L3/L2 white-line intensity ratio (second derivative method) reveals a dominance of magnetite Fe3O4.

The $I_3/I_2$ white-line intensity ratio for the 3d transition metals and the $M_2/M_4$ white-line intensity ratio for the rare earth metals can be used as a sensitive probe of the local oxidation state in oxides of these elements. Results from two systems are described. For ceria (nominally CeO$_2$) samples obtained by mechanical polishing (CMP), electron energy-loss spectroscopy (EELS) measurements recorded as spectrum lines in STEM mode have revealed that the surfaces of the nano-particles are reduced through the segregation of oxygen vacancies to the surface and through Ce adopting a trivalent state, or through a combination of the two mechanisms. The high concentration of oxygen vacancies accompanying the near-surface reduction in cation valence is expected to play an important role in CMP. The increase in the Ce $M_2/M_4$ white-line intensity ratio from Ce$^{3+}$ to Ce$^{4+}$ is accompanied by a reduction in binding energy of 1 eV and significant changes in the shape of the white lines. The oxygen electron energy-loss near-edge structure (ELNES) also exhibits dramatic changes. The results are compared with x-ray absorption spectra of ceria in various oxidation states. Spectrum lines of Co L$_2$ and oxygen ELNES have been recorded in the TEM mode at a resolution of 1 nm across colloid oxide periclase (CoO) - spinel (Co$_2$O$_3$) interfaces, with the use of an image-forming slit in a Gatan image filter (GIF). The increase in $I_2/I_1$ white-line intensity ratio in going from the mixed Co$^{2+}$ and Co$^{3+}$ of the spinel structure to the Co$^{2+}$ of the periclase structure is accompanied by a binding energy reduction of 1.3 eV and subtle changes in the shape of the white lines. Dramatic changes in the oxygen ELNES are also observed. Interestingly, recent reanalysis of the Co L$_2$ ELNES by multivariate statistical analysis reveals a spectrum that is not well modeled by a linear combination of spectra from CoO and Co$_2$O$_3$. It is expected that high-resolution ELNES data recorded with a monochromated field emission gun analytical electron microscope will provide additional insight and sensitivity for these localized changes in valence and bonding. Research at the ORNL ShuRE User Center supported by the Division of Materials Sciences and Engineering, Office of Basic Energy Sciences, U.S. Department of Energy, under contract DE-AC05-00OR22725 with UT-Battelle, LLC.
mechanical properties of the material. Oxide-rare-earths/Si3N4 interfaces were studied by atomic-resolution electron energy loss spectroscopy (A-ERELS) and Z-contrast imaging in a scanning transmission electron microscope (STEM). In particular, the following oxide-rare-earth intergranular phases: La2O3, Sm2O3, Er2O3, Yb2O3 and Lu2O3 were examined at the interface with the matrix oriented along the zone axis [0001]. We discovered a direct correlation between the fracture toughness and the atomic position of rare-earth atoms at the interface. Z-contrast images show that the position of rare-earth atoms at the interface is predominantly controlled by their atomic radius. In the case of La, which has the largest shell radius of the rare-earth elements, does not segregate at the interface with a specific structure. While for Sm, Er, Yb and Lu the bonding at the interface is periodic and occurs at very specific positions. Sm atoms, the second largest shell radius bond to the oxygen at the center and at the termination of the open hexagonal Si3N4 rings. For smaller radii, the atoms bond in pairs only at the termination of the open rings. This is the case for Er, Yb and Lu. The density of atoms at the termination position increases with decreasing atomic radius of the shell radius from Er to Lu. Atomic resolution EELS taken at the interface suggest that the electronic structure of the rare-earth dopants plays a secondary effect on the positioning of the atoms at the interface. Furthermore, the Si L2,3 edge signal from the termination position has Si-O-like features indicating that the open hexagonal Si3N4 rings are oxygen terminated. Fracture toughness measurements were performed on La, Sm and Lu doped samples. The La samples follow the Sie discussion properties than the Sm and Lu samples; while the Lu samples present the best mechanical properties. In conclusion, our results indicate that oxygen and the density of rare-earth atoms at the termination of the open hexagonal Si3N4 rings are essential and determinant the mechanical properties of Si3N4.

4:30 PM P2.10
High-Resolution Interface Atomic Structure Analysis in Silicon Nitride Ceramics. Alexander Ziegler1,2, Juan C. Idrabo3, Raphaelle L. Satet4, Michael J. Hoffmann4, Michael K. Cinibulk5, Ritchie1,7, lMaterials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California; 2Department of Chemical Engineering and Materials Science, University of California, Davis, Davis, California; 3Physics Department, University of California, Davis, California; 4IKM, University of Karlsruhe, Karlsruhe, Germany; 5Materials Directorate, Air Force Research Laboratory, Wright-Patterson Air Force Base, Ohio; 6National Center for Electron Microscopy, Lawrence Berkeley National Laboratory, Berkeley, California; 7Department of Materials Science and Engineering, University of California, Berkeley, California.

Silicon nitride ceramics consist of elongated Si3N4 matrix-grains that are randomly oriented and interlocked, and most intergranular phase secondary phase; the intergranular phase. This intergranular phase materializes mostly as a very thin, amorphous film between the matrix grains, just about one nanometer in thickness, and especially its chemical composition and bonding characteristics are critical to the mechanical properties. Indeed, these intergranular films need to be engineered in order to control material integrity, strength, and fracture toughness. In the past this was done empirically by imposing compositional details to the intergranular phase about the intergranular atomic structure and bonding characteristics. For the present study we have the capabilities to access this critical information and we investigate how different rare-earth atoms bond to the interface differently depending primarily on atomic size. Elements with the smallest atomic radius (Lu) appear to attach to the Si3N4 prism plane in pairs. As the atomic radius becomes larger these pairs separate more (Yb, Er), attaching then as single atoms to the interface (Sm). The largest among (La) does not show any preference for bonding to a particular atomic site along the interface. A corresponding radius size effect can be observed on the fracture toughness of these ceramic compositions, ranging from low toughness for the La containing material to high toughness for the Lu doped material. EELS measurements identify: (i) identical bonding characteristics for single Sm atoms on the two atomic positions it attaches to along the interface, and (ii) the prism planes appear to be oxygen terminated.

4:45 PM P2.11
In Situ Quantitative Plasmon Spectroscopic Determination and Interpretation of Solid-state Properties at the Nanoscale: A New Capability for Material Research. Vladimir P. Oleshko and James M. Howe; Materials Science and Engineering, University of Virginia, Charlottesville, Virginia.

Plasmons generated by fast electrons passing through any solid enable one to probe materials properties that are governed by ground-state densities because their energy, Ep, is related to the valence electron density, n, as Ep = (e2/(2m*p))1/2 + E0 + 2E0n1/2. Here n = (ε[ne2/(ε0m*p)]1/2 is the free electron plasma frequency, ε is the electron charge, E0 is the permittivity of vacuum, m is the electron mass, and E0 is the bandgap energy. Furthermore, we have established universality and scaling in relations between Ep, electron density, n, and the boundary of Wigner-Seitz (WS) cells and equilibrium lattice cell calculated elastic constants and hardness for a number of single crystal and polycrystalline materials, nonmetals, metalloids and compounds that follow the universal binding energy relation (UBER). Its origin lies in the nature of electron-ion (atomic nuclei) interactions and in the exponential decay of n with interparticle separation, or into interstitial sites, since the scaled cohesive energy, Ep = /Ecoh, atomic separation, a = (ε0Ecoh/4π)1/2, is the equilibrium cohesive energy, Ecoh, is the equilibrium interatomic spacing) can be described by a Rydberg type function, E*(a*) = (1 + (a*/a)2)−1−(1−/a)2. The density scaling is defined here as, n = (1/(4π)1/2)−3/Ecoh, where r = Ecoh is the equilibrium WS atomic radius, is the characteristic length describing the width of the binding energy curve and a = (ε0Ecoh)1/2 is the anharmonicity parameter. As a consequence, we found a strong scaling of Ecoh/r and elastic constants with Ep and we are able to measure the rare-earth elements, does not segregate at the interface with a particular atomic site along the interface. A corresponding radius size effect can be observed on the fracture toughness of these ceramic compositions, ranging from low toughness for the La containing material to high toughness for the Lu doped material. EELS measurements identify: (i) identical bonding characteristics for single Sm atoms on the two atomic positions it attaches to along the interface, and (ii) the prism planes appear to be oxygen terminated.

SESSION P3: Poster Session: Electron Microscopy of Molecular and Atom-scale Mechanical Behavior, Chemistry, & Structure
Chairs: David Muller and Eric Stach
Monday Evening, November 29, 2004
8:00 PM Exhibition Hall D (Hynes)

P3.1 Progress towards using electron holography as a quantitative dopant profiling technique. Dave Cooper, Alison Twitchett, Rafal Dunin-Borkowski and Paul Midgley; Materials Science, University of Cambridge, Cambridge, United Kingdom.

A range of techniques has been used to prepare Si and GaAs based semiconductor devices for examination using electron holography. Combinations of cleaving, focussed ion beam milling and Ar-ion milling have been used to prepare samples with thicknesses in the range 200-500nm. Off-axis holograms have been acquired at 200kV using a Philips CM300 FEGTEM, the relative effects of the sample surface on the measured phase shift have been assessed. Details of these results will be presented.

P3.2 Simulations of the electrostatic potential in a thin silicon specimen containing a p-n junction. Philippa Somodi1, Rafal E. Dunin-Borkowski1, Alison C. Twitchett1, Crispin H. W. Barnes2, Jane E. Smiley3, 4Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California; 2Department of Materials Science and Engineering, University of Cambridge, Cambridge, United Kingdom; 3Department of Physics, University of Cambridge, Cambridge, United Kingdom.

Off axis electron holography allows the phase shift of an electron wave that has passed through a thin specimen to be recorded directly in the transmission electron microscope (TEM). The measured phase shift can be related to the electrostatic potential. Previous electron holography studies have shown that built-in potentials across semiconductor p-n junctions in thin TEM specimens are usually lower than predicted and the value measured is highly dependent on the sample preparation technique. This work uses finite element methods to solve the standard semiconductor equations in order to calculate...
the potential throughout two- and three-dimensional specimens. The effect of the finite sample thickness and sample preparation can be modelled by comparing the simulation results. The lower built-in potential measured in experiments can be partially accounted for by the electronic surface states on the specimen, which will have a more dominant effect for thinner specimens.


The catalytic activities of Au/TiO2 nano-hetero catalysts depend on their nanostructure and show the size dependence, and the support dependence. The mechanism of the catalytic activities of gold nano particles, the size dependence and the support dependence are considered to be different to the one on the substrate and near the interface between the gold particles and the oxides. The large size of the gold particle was over 5nm, the mean inner potential of gold was the same as that of bulk Au. When the size is below 5nm, the mean inner potential became to increase. Further, the mean inner potential of gold increased depending on the size of the particle. When the size of the gold particle is over 5nm, the mean inner potential of gold was the same as that of bulk Au. When the size is below 5nm, the mean inner potential became to increase. It increases suddenly over 40V, particularly in case of below 2nm. It is considered that the electronic state of nano Au/TiO2 catalysts is different from that of bulk state as the size decreases. On the other hand, the mean inner potential of gold in Au/TiO2 catalysts prepared by VE method also increased as the size decreased, but the behavior of the size dependence is different from that of DP method. The critical size of the mean inner potential change is around 3nm. The size of the gold particle was below 3nm, the mean inner potential of gold increased gradually. The mean inner potential of VE method is less than that of DP method with the same particle size in spite of the size below 3nm. The stoichiometry at the interface between Au and TiO2 should be considered to have relation to the change of the electronic state near the interface. The mean inner potential of VE method is less than that of DP method. The TiO2 supports prepared by DP method and VE method can be simply calculated by free electron model, i.e., Drude model, in the particle. When the size of the gold particle is over 5nm, the mean inner potential of gold increased depending on the size of the particle. When the size of the gold particle is over 5nm, the mean inner potential of gold increased depending on the size of the particle.

P3.4 High Spatially Resolved EELS Imaging Technique for Plasmon Loss Energy Distribution Measurement in Amorphous Aluminum Oxide Thin Films, Mitsuaki Koida, Hiroki Tanaka, Mitsuhiro Tomita and Shiro Takeno; Corporate Research & Development Center, Toshiba Corporation, Yokohama, Japan.

Objective: The STEM/EELS imaging technique is emerging as a key technique for material science. High-energy resolution with sufficient high-spatial resolution measurement technique is strongly required in the next-generation semiconductor research. In previous studies, many mapping imaging and evaluation of composition and chemical bonding states were obtained by the energy filtering (EF) method with EF-TEM. However, it is unsuitable for detailed evaluation since overall energy resolution of the EF image strongly depends on the width of the energy selecting slit, which is ordinarily greater than 1eV. We developed a high energy resolution Spatially Resolved EELS (SREELS) technique and show a new finding concerning the subtle fluctuation of mass density in amorphous Al2O3 thin films.

Experimental: We evaluated the amorphous Al2O3 thin films deposited on silicon substrate by a sputtering method. Cross-sectional TEM specimens were prepared by mechanical and ion-beam thinning methods. The line scan EEL spectra from the top surface of the film to the adjacent Au film were acquired using a Gatan Model 666 (Gatan Model 666) attached to a FE (Field Emission)-TEM (HF-2000). Each spectrum was obtained at a dispersion of 0.05 eV/channel, 50 ms duration and intervals between adjacent analytical points were 0.2 nm for estimating the low-loss region. Furthermore, the intensity of each spectrum was normalized on the basis of plasmon loss peak height, and measured spectra were reconstructed as 2D (depth position of the film vs. loss-energy) image. Results and discussion: We obtained 2D EF-STEM images of Al2O3 thin films, and observed clear fluctuation of plasmon loss peak energy, within the range from 22.5 eV to 28.0 eV in Al2O3 thin films. It is well known that plasmon energy can be simply calculated by free electron model, i.e., Drude model, in metallic materials. Even if the specimen is insulating, W. Tews and R. Gr n德尔 pointed out that the Drude model can be adopted for three modifications of Al2O3. They revealed the relationship between valence electron density and plasmon loss energy. It also suggested that we can evaluate the mass density p by measuring the plasmon energy using Bell's model. The mass density of the upper region of the film is estimated to be 0.1 g/cm3 higher than that of the lower one. The detection limit of density fluctuation (Δp) in our method was approximately 0.1 g/cm3 and energy resolution were 0.2 nm and 0.5 eV, respectively. Conclusion: We developed a visualization method of the fluctuation of plasmon energies in a small area of interest, and found slight changes of the mass density in Al2O3 thin films deposited on silicon substrate. The fluctuation of plasmon loss peak energy was observed by measuring the plasmon energy within the range from 22.5 eV to 28.0 eV. The plasmon loss peak energy increased suddenly over 40V, particularly in case of below 2nm. The mean inner potential of VE method is less than that of DP method with the same particle size in spite of the size below 3nm.
Series of Ferrimagnetic Bioglass Ceramics (FBC) were prepared in the system of oxides \([0.45(\text{CaO})_2\text{P}_2\text{O}_5(0.52-x) \text{SiO}_2\text{Fe}_{2\text{O}_3}0.03\text{Na}_2\text{O}])\), where \(x = 0.05, 0.10, 0.15, 0.20\). The materials were characterized by using x-ray diffraction (XRD), scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS) and X-ray fluorescence (XRF) measurements. A strong correlation between processing parameters, structure, microstructure and magnetism was discovered. Bioactivity studies from all systems will be discussed.

The interdendritic region appears very porous while the size of the pores is increasing with the time of immersion. Results of the surface studies from all systems will be discussed.

### P3.9

**Correlation Microscopy: Where Light Microscopy Meets Cryo-Electron Microscopy**

Anna Sartori; Juergen Plitzko and Wolfgang Baumeister; Molecular Structural Biology, Max Planck Institute for Biochemistry, Martinsried, Germany.

Cryo-electron microscopy of frozen, hydrated, living samples on carbon-coated grids is a powerful technique for investigating the structure of quasi-living cells with nanometer-scale resolution. A major inconvenience of this method is due to the fact that the applied high magnification implies a long and not always fruitful search for the structures of interest and does not always enable the experimenter to unequivocally identify the nature of the part of the sample being imaged. Additionally, time-scale experiments are almost impossible, due to the lack of information of the dynamic state during plunge-freezing. A way to tackle this problem consists of determining the position of the area of interest directly on the TEM (Transmission Electron Microscopy) grid by imaging it using light microscopy, prior to investigating it with cryo-electron microscopy. In the first stage, we succeeded in building a prototype of a cryo sample-holder for a fully automated Zeiss Axiostar 200M microscope and long working distance objectives (20x and 40x magnification). Fluorescently-labeled neurons grown on carbon-coated TEM-grids, have been embedded in vitrified ice and used for first studies. The sample is kept at all times at liquid nitrogen temperature by being placed in a liquid nitrogen atmosphere on a copper holder which is currently being built as a more sophisticated sample holder, presenting reduced condensation effects at the glass cover slip and improved temperature control to prevent contamination of the frozen sample (by crystalline ice and dirt particles). This second generation holder will ensure higher resolution and reproducible working conditions. A key objective is the possibility of transferring the coordinates of the area of interest, found on the frozen grid, directly from the light microscope to the electron microscope. MatLab-based software is being currently used to transform the coordinates of the areas of interest, found on the light microscopy images, to the electron microscopy images. This whole procedure allows to speed up the sample investigation steps considerably and, moreover, it provides invaluable guidance in the identification of the imaged objects.

### P3.10

**Transmission electron microscopy study on the domain structures in ferroelectric SrBi_2Nb_2O_9 ceramics**

K. Chinnanthambi, Ravishankar Narayanan and K.B.R. Varma; Materials Research Centre, Indian Institute of Science, Bangalore, India.

A transmission electron microscopy study has been carried out on the domain structures of SrBi_2Nb_2O_9 (SBN) ferroelectric ceramics which belong to the Aurivillius family of Bi-layered perovskite oxides. SBN is a potential candidate for NVRAM applications. The ferroelectric domains and antiphase boundaries (APBs) were identified with dark field imaging techniques using different superlattice reflections which arise as a consequence of octahedral rotations and cationic shifts. The domain walls are irregular in shape due to the lack of information of the dynamic state during deposition of the sample. Antiphase boundaries are less dense and are connected to that of SrBi_2Ta_2O_9. The electron microscopy observations are correlated with the polarization fatigue nature of the ceramic where the antiphase boundaries possibly play a key role in the fatigue free behavior of the Aurivillius family of ferroelectric oxides.
of bcc metals and alloys. Simulations have also shown that non-shear stress alters the core structure by changing the edge displacements of the core atom. Mapping these edge displacements is therefore extremely useful in predicting the response of a screw dislocation to the orientation of the applied stress. In this work, High Resolution Electron Microscopy (HREM) images are simulated using the multislice method to determine the atomic motions and electron optical parameters on the appearance of the edge displacements for screw dislocations in bcc molybdenum. The dislocation configurations used in the simulations are based on atomic and first principle calculations. In addition, surface relaxation of the foil (i.e. the Eschelby twist of a screw dislocation), which complicates experimental observation of the true core structure, is also separately simulated for the ideal case of isotropic elasticity. The multislice simulations will then be compared with experimental images of the dislocation core.

P3.14
On the Effect of Local Grain-Boundary Chemistry on the Macroscopic Mechanical Properties of a High Purity Y2O3-Al2O3-Containing Silicon Nitride Ceramic: Role of Oxygen. Alexander Ziegler, James M. McNaney, Michael J. Hoffmann and Robert O. Ritchie; 1Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California; 2Materials Science and Technology Division, Lawrence Livermore National Laboratory, Livermore, California; 3IKM, University of Karlsruhe, Karlsruhe, Germany; 4Department of Materials Science and Engineering, University of California, Berkeley, California.

The effects of grain-boundary chemistry on the mechanical properties of high purity silicon nitride ceramics have been investigated. These effects are specifically involving the role of oxygen, present along the grain boundaries, in influencing the fracture behavior. To avoid complications from inadvertently introduced impurities, studies were performed on highly crystalline, single-phase silicon nitride, either using two-step gas-pressure-HIP sintering. Varying the grain-boundary oxygen content, which was achieved by control of oxidizing heat treatments and sintering additives, was found to result in a transition in fracture mechanism, from transgranular to intergranular fracture, with an associated increase in fracture toughness. Transmission electron microscopy of the microstructure and detailed EDS measurements on the thin intergranular films and the triple junctions revealed that this phenomenon is accompanied by an oxygen-induced change in grain-boundary chemistry and possibly to a concomitant structural transformation along the interface. The incorporation of oxygen appears to affect fracture by weakening the interface, thus facilitating decohesion and crack advance along the boundaries, and hence to toughening by grain bridging. It is concluded that if the oxygen content in the thin grain-boundary films exceeds a lower limit, which is 0.87 equiv% oxygen content, then the interfacial structure and bonding characteristics favor intergranular decohesion during crack propagation; otherwise, transgranular fracture ensues.

P3.15
Interfacial Atomic and Chemical Structure of Pt Thin Films Grown on SrTiO3 (111) Substrates. Ju-Hyung Suh, Yong-Seok Lee and Chan Gyung Park; Materials Science & Engineering, Pohang University of Science & Technology (POSTECH), Pohang, Gyeongbuk, South Korea.

Pt thin film has a useful application for electrodes of advanced memories, such as FeRAM, MRAM, PRAM, and so on. Due to similar structural characteristics, such as lattice parameter and crystal structure (Pt=0.3952nm, fcc; SrTiO3=0.3905nm, perovskite), SrTiO3 is the most applicable material for epitaxial Pt growth. In addition, SrTiO3 can be applied to buffer layer for stable growth of various oxide thin films due to interfacial stability. Pt and SrTiO3, and Si. Therefore, the interface between Pt and SrTiO3 should be a considerable research area for improvement of Pt and SrTiO3 growth characteristics. Compared with many researches for interface between Pt and SrTiO3 substrates, this study is an undeveloped area and has an important role for basic data for the electronic device development. The study on the interfacial structure between Pt and SrTiO3 (111) substrate is performed on in-situ heating TEM analysis. Second, in progress, interfacial atomic arrangement between Pt and SrTiO3 (111) has been investigated by using high resolution electron microscopy (HREM) and HREM simulation. Third, chemical state between Pt and SrTiO3 (111) has been investigated by using energy loss near edge structure (ELNES) and ELNES simulation.

P3.16
Abstract Withdrawn
The discrete A). Trueimage~ have been filtered transmission electron microscopy (EFTEM). The principal for cubic nanocrystals with lattice constants larger than 0.4 nm, scanning transmission electron microscopy (STEM) and energy systems there are biological structures where the alternative imaging such applicability as well as a discussion of the practical problems and examination of functional nanostructures, where the relationship exist whose lifetime is long enough to be recorded - in this case, cryoelectron microscopy of ribosomes. [3] J. Frank (2003) Electron microscopy of functional ribosome complexes. Biopolymers 68, 223-233.

Since the crystallographic phase and morphology of many materials changes with the crystal size in the ten nanometer range and the potential technological applications of nanoparticles are enormous, a need arises to determine the crystallography of nanoparticles individually. Direct space high-resolution phase-contrast TEM and atomic resolution Z-contrast scanning TEM when combined with goniometry of direct lattice vectors offer the possibility of developing dedicated nanophotography characterization methods for such small nanoparticles. The opportunistic tilt strategy for determining the lattice parameters of individual cubic nanocrystals from only two high-resolution electron phase-contrast images recorded in contemporary TEMs with a modest tilt range is reviewed. In future aberration-corrected TEM, more elaborate tilt strategies become possible and most nanocrystals with lower than cubic symmetry can be characterized. Although experimentally feasible in contemporary high-resolution TEMs with modest tilt range for cubic nanocrystals with lattice constants larger than 0.4 nm, transmission electron goniometry has so far only been employed by a few specialists. This is likely to change with increased availability of aberration-corrected TEMs. Supported by dedicated nanocrystallography software and computer controlled specimen goniometers with an additional degree of freedom to tilt the specimen, the characterization of all kinds of nanoparticles (cubic and non-cubic) will become practical on a day to day basis.

The technique of electron tomography has, in recent years, broadened its application into materials science through the application of novel imaging and tomographic techniques such as dark field scanning transmission electron microscopy (STEM) and energy filtered transmission electron microscopy (EFTEM). The principal goal of these early studies was to show the development of technique and demonstrate possible applications. Now that the use of these tools is becoming more routine the emphasis is moving towards their application in the solution of structural problems which are intractable to traditional, two dimensional, techniques. Results will be presented of several such studies. These will include the examination of the precise morphological transformation involved in the activation of iron/iron oxide catalysts supported on nanostructured silica, combined with conformation of oxidation states by electron energy loss spectroscopy. These results will be presented on the examination of functional nanostructures, where the relationship between precise 3D morphology and chemistry is key to performance. The biological sciences originally developed electron tomography, using bright field TEM, to examine the structure of biological macromolecules. While bright field contrast is ideal for many such systems there are biological structures where the alternative imaging approaches, originally used for inorganic systems, generate contrast which is a weak signal, not superior for tomography. Examples include high Z inclusions inside cells (HAADF) and the location of functional chemicals (EFTEM). Results will be presented to confirm such applicability as well as a discussion of the practical problems and challenges which need to be overcome to achieve such results.

Low-resolution tomography requires recording images every few degrees. As a consequence, the sample is often degraded after such a procedure. However the required input can be reduced drastically by using knowledge about the position and the number of atoms in each structural element. This concept has been tested in the present investigation where HREM image simulation (MacTempus) together with exit wave reconstruction (FEI TrueImag) have been performed. A cubocephalid nanoparticle is used for the simulation with different compositions i.e., pure solid Ga and In-Ga and hollow Ga particles. Six different zone axes ([111], [111], [001], [110], [110], [001]) have been used and the data is obtained by a corrected microscope (200 kV, Cs = 0 nm, resolution = 0.5 Å). The discrete grid data were determined by constructing a channeling map from the reconstructed exit wave images. In this special case only three projections [001], [110], [110] were sufficient to find a unique volumetric reconstruction, illustrating the potential of the method. The other projections were used for checking the solution. The comparison between the projected potentials (simulated input) and the final result shows that discrete tomography reconstructs the exact projection of all 209 atomic planes of the 3D shape of the nanoparticle. Additional results and limitations of the method as well as requirements for performing the real experiment will be discussed.

Three-Dimensional Characterization of the Structural Properties of Quantum Dots. Ilke Arslan1, Timothy J. V. Yates1, Matthew Weyland2, Paul A. Midgley2 and Nigel D. Browning2
1Department of Materials Science and Metallurgy, University of Cambridge, Cambridge, United Kingdom; 2Department of Applied and Engineering Physics, Cornell University, Ithaca, New York; 3Department of Chemical Engineering and Materials Science, University of California at Davis, Davis, California.

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Discrete Tomography of Ga and InGa Particles from HREM Image Simulation and Exit Wave Reconstruction. Joerg R. Jinschek1, Joost Batenburg2, Hector Alfredo Calderon4, Dirk Van Dyck5, Fang R. Chen5, Velimir Radmilovic5 and Christian Kisielowski1
1National Center for Electron Microscopy, Ernest Orlando Lawrence Berkeley National Laboratory, Berkeley, CA, California; 2Mathematical Institute, Leiden University, Amsterdam, Netherlands; 3Chemistry, University of Illinois at Urbana-Champaign, Urbana, Illinois; 4Materials Science & Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois; 5Center of Electron Microscopy, National Tsing Hua University, HsinChu, Taiwan.

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The success of future applications of metal nano-clusters in heterostructures has been harnessed in nanomaterials and graphene technology. As the nano-clusters become smaller, completely different catalytic activity has been observed in some systems, such as Pt-Ru and gold nanoparticles. Yet, the 3-dimensional structure and composition of these supported nano-clusters is still challenging to be quantified by conventional methods due to their limitations in understanding size distribution of supported metal nanoclusters that are generally less than 5 nm. Here, we demonstrate our novel method to determine the number of atoms in very small clusters, such as Re6 and PtRu5 nanoparticles [3], using this novel mass spectroscopic technique [4]. In this work, we present the applications of this novel HAADF imaging, combined with lattice imaging in high-resolution electron microscopy (HREM) in determining 3-dimensional structure and dynamics of supported metal nanoparticles. Two classes of model materials were chosen as supported metal nanoparticles, i.e., ligand-protected Au13 nano-clusters and graphite-supported Pt nanoparticles. Ligand-protected Au13 nano-clusters provide experimental control of nanoparticle size and local environment defined by the choice of ligand, while graphite-supported Pt nanoparticle offers great access to dynamical studies of cluster growth and structural evolution. A large amount of TEM data has been collected from the newly synthesized size-controlled gold particles, which have been shown by TEM to be of sub-nanometer size (0.84 nm) and highly monodisperse narrow distribution. Current efforts are focused on unambiguously identifying the size and composition of these TEM data to that obtained at the level of the ensemble using x-ray spectroscopy, which shows polymorphism and unique structure of Au13 clusters. In the meantime, the similar analysis procedure is currently being performed for graphite-supported Pt nano-clusters [2].

3:00 PM P5.5
Electron Holography as a Tool for Dopant Profile Characterization of Semiconductor Devices, Takao Matsumoto and Masanari Kooguchi, Central Research Laboratory, Hitachi, Ltd., Kokubunji, Tokyo, Japan.

Electron holography [1] is a promising tool for distinguishing the dopant profile in a MOS transistor [2, 3], especially for devices using light dopant atoms such as borons. This is because it is the electrostatic potential of the specimen itself that is to be measured in electron holography rather than the density of the dopant atoms. Therefore, it is possible to describe the dopant profile as a detectable electrostatic potential distribution in two dimensions by applying a high voltage to the specimen. Future nanostructures are produced in a highly spatial resolution of the method compared with other possible dopant profiling techniques, which is advantageous. In order to show the advantage of our technique, several problems must be overcome. For example, it is necessary to prepare a thin film specimen of uniform thickness from a bulk wafer. Secondly, the sensitivity of electron holography itself must be improved as much as possible. Also, electron beam induced charging of the sample must be eliminated, and the surface must be precisely controlled. To overcome the first obstacle, we have used an FIB system with a modified beam scanning scheme in which a high-frequency analog modulation signal is added to the digital signal of the beam deflector. This has enabled us to smooth the residual surface roughness presumably caused by the glitch-noise of D/A converters and we have observed a very atomically smooth surface was obtained as estimated with an AFM. Also, we have tried to maximize the quality of holograms using a 300-kV cold-field emission microscope (HF-3000) using an optimized elliptical illumination. The overall performance of the microscope has been confirmed by recording a maximum of 16,000 numbers of electron interference fringes on a conventional electron microscope film [4]. Fine modulation of the electron interference fringes thus recorded on a film was digitized, taking advantage of the state-of-the-art film scanner using a sophisticated optical system with 16-bit resolution. We used this optimized system to characterize the dopant profile in MOS transistors, and comparisons with the calculated profiles from device simulation have shown that our model is in good agreement. [1] A. Tombolato, Electron Holography, 2nd ed. (Springer, Heidelberg, Germany, 1999). [2] Rau W. D., Schwander P., Baumann F. H., Hoppner W., and Ourmazd A., Phys. Rev. Lett. 82 (1999) 2614. [3] Gribovskiy M. A., McCann M. R., Li J., Murthy C. S., Ronheim P., Doris B., McMurray J. S., Hedge S. and Smith D. J., Phys. Rev. Lett. 80 (1998) 25502. [4] T. Matsumoto, et al., to be published.

2:15 PM P6.3
Three-dimensional analysis of the dopant potential of a silicon p-n junction, Alison Twitchett, 1 Rafael Dunin-Borkowski 1, Simon Newcomb 2 and Paul Midgley 2, 3 Materials Science, University of Cambridge, Cambridge, United Kingdom; 2Sonas Ltd, Glebe Laboratories, Newport, Co. Tipperary, Ireland.

Dopant profiling of semiconductor devices using off-axis electron holography has become more widely used in recent years, with many examples of the successful visualisation of dopant-related electrostatic potentials. Electrically biased holography experiments have also been carried out in-situ in the electron microscope in order to ensure that the device is examined under conditions that are as close to working conditions as possible [1]. Although electron holography promises to provide full quantitatively meaningful results, the measurement of a two-dimensional projection along the electron beam direction through the semiconductor membrane thickness, thereby including all surface potential effects. These surface contributions are of particular interest when using electron holography to examine semiconductor device structures because focused ion beam (FIB) milling is required for site-specific membrane preparation of current generations of devices. This preparation technique is known to generate substantial amorphous and electrically altered surface layers three-dimensional
characterisation of the electrostatic potential within a transmission electron microscope (TEM) membrane is required to reveal such surface effects, information which can be obtained through the use of electron tomography. Electron tomography involves the use of a high angle tilt series of images to reconstruct three-dimensional information about a sample, and has been applied successfully to the examination of small particles such as catalysts. However, this technique has not yet been applied to electrostatic potential variations such as those found in semiconductor devices. By using a custom-built two-contact electrical biasing holder [2], electron tomography and electron holography experiments have been combined to investigate the three-dimensional potential distribution in a semiconductor device. A silicon wafer containing a p-n junction was prepared using FIB milling into a geometry suitable for high tilt experiments. Electron holograms were acquired at tilt angles of up to 76° in a Philips CM300 TEM, both with and without applied forward and reverse electrical bias. A detailed description of the experimental procedure will be presented, along with both experimental and simulated results of the potential distribution within the device. [1] A. C. Twibell et al., J. Microsc. 214, 3, 287-296 (2004) [2] R. E. Dunin-Borkowski et al., Paper presented at Microscopy and Microanalysis 2004.

3:00 PM *P5.4
Experimental Demonstration of Diffractive Imaging in Electron Microscopy using A Complex-valued Amorphous Object. Zhongyi (Vie) Liu1, Dean J. Miller1, J. Tao2, J. M. Zuo2 and S. Marchesin2,3 Materials Science Division, Argonne National Laboratory, Argonne, Illinois; 2Department of MS&E and the Center for Microanalysis of Materials, Frederick Seitz Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois; 3Department of Physics and Advanced Technologies, Lawrence Livermore National Laboratory, Livermore, California.

Numerically reconstructing an object (image) from its diffraction intensity based on oversampling and iterative algorithms, i.e., diffractive imaging, has provided the capability for lens-aberration-free diffraction-limited imaging. Until now diffractive imaging in transmission electron microscopy has been thought to be difficult (if not impossible) unless the object is real-valued and nonnegative or has a special support. The reason for this is that the object to be reconstructed is complex-valued in general and hence a tight support, i.e., the true boundary of the object, is a prerequisite for iterative algorithms to converge. However, the tight support is often difficult to obtain. In this work, we have utilized new development in determining the support to circumvent this paradox. We used a method based on Patterson function and Fienup's hybrid input-output algorithm to obtain a good, although not necessarily exact, estimate of the support. We then used a RAR (relaxed averaged Alternating reflections) algorithm to improve the image reconstruction. Our results show that the reconstruction of a complex-valued amorphous object appears to be achievable from its diffraction intensity with no need for a priori knowledge of the support. We propose that diffractive imaging in electron microscopy has the potential for many applications in 2- and 3-dimensional imaging where resolution, contrast, radiation damage, and sample drift, etc. become critical effect(s) on image quality.

3:45 PM P5.6
Accurate Determination of Orientation Relationships between Ferroelastic Domains: The Tetragonal to Monoclinic Transition in LaNbO₄, as an Example. Osysten Prytz and Johan Tafto; Centre for Materials Science and Nanotechnology, University of Oslo, Oslo, Norway.

LaNbO₄ crystallizes in a tetragonal high-temperature phase with space group I₄₁/a, which transforms to a monoclinic phase upon cooling below 500 °C. The low-temperature phase has space group I₂₁/m with a monoclinic angle 52°94'. This system serves as a useful model of a ferroelastic transition of the P₄m/n to m type using the notation of Aizu [1]. This transition produces ferroelastic domains, the boundaries between which are parallel to the monoclinic a- and c-axes. The orientation of these boundaries relative to the monoclinic a- and c-axes has been predicted by Sapiro [2] for all 34 ferroelastic species, and calculations specifically for the LaNbO₄ system have been presented by Jian and Wayman [3]. We present an accurate determination of the boundary orientation in LaNbO₄ using electron diffraction with a parallel beam. The boundary planes are parallel to the (2 0 -5.10)/(5.10 0 2) planes of the two domains, as opposed to the predictions of Jian and Wayman which indicate that the domain boundaries should be oriented parallel to the (2 0 4.04) planes. Our experimental results are in good agreement with the results of a previous study [4]. Furthermore, we present a simple geometric model for calculating the boundary orientation based only on the unit cell parameters of the monoclinic phase. This model gives a boundary orientation in excellent agreement with our experimental determination. References [1] Aizu, Phys. Rev. B 2, 754-772 (1970). [2] J. Sapiro, Phys. Rev. B 12, 5138-5140 (1975). [3] L. Jian and C. M. Wayman, J. Am. Ceram. Soc. 79, 1662-1668 (1996). [4] S. Tsueikawa and H. Takai, Phys. Stat. Sol. (a) 50, 695-702 (1978).

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4:00 PM P5.7

A very unusual microstructure has been found in tantalum thin films after transformation from the tetragonal β phase to the bcc α phase. The β phase is a metastable structure that is found only in thin films deposited under certain conditions. Films deposited in the β phase transform to the stable α phase when heated to sufficiently high temperatures. The microstructure of completely phase-transformed films has been studied using electron backscatter diffraction (EBSD)
Electron Microscopes (FEG TEM) in recent years has been found to decrease monotonically with increasing annealing temperature. Structure characterization will be discussed.

Segregation binding energy, which was thus measured to be -0.021 eV/atom, has thermodynamic properties similar to a bulk hcp phase. In a face-centered cubic alloy dislocation produces a stacking fault that has a different crystallographic environment compared to the rest of the crystal. The difference in chemical potential will therefore give rise to solute segregation or desegregation to the stacking fault plane, the sense of the solute redistribution being governed by the need to lower the entropy of the metastable stacking fault. This is called Suzuki segregation. Since Suzuki segregation alters the stacking fault energy of the alloy, the phenomenon has an important effect on the mechanical properties, such as the work hardening rate and creep strength at elevated temperatures. However, the extremely localized nature of the segregation (of the order of the stacking fault thickness, which is two interplanar spacings thick) makes it hard to detect Suzuki segregation experimentally. Nevertheless, the development of Field Emission Gun Transmission Electron Microscopes (FEG TEM) in recent years has largely overcome this difficulty. We have used a FEG TEM to measure the local composition across stacking faults in a Cu-7.15 at% Si alloy annealed at various temperatures. A silicon enrichment, due to the segregation of silicon to stacking faults, was observed at the stacking fault plane and was found to decrease monotonically with increasing annealing temperature. This temperature dependence was used to determine the segregation binding energy, which was thus measured to be -0.021 ± 0.019 eV/atom. This value does not compare favorably with the theoretical estimate calculated from bulk phase diagrams, which overestimates the binding energy.

Suzuki Segregation to Stacking Faults in a Cu-Si Alloy.

In a face-centered cubic alloy dislocation produces a stacking fault that has a different crystallographic environment compared to the rest of the crystal. The difference in chemical potential will therefore give rise to solute segregation or desegregation to the stacking fault plane, the sense of the solute redistribution being governed by the need to lower the entropy of the metastable stacking fault. This is called Suzuki segregation. Since Suzuki segregation alters the stacking fault energy of the alloy, the phenomenon has an important effect on the mechanical properties, such as the work hardening rate and creep strength at elevated temperatures. However, the extremely localized nature of the segregation (of the order of the stacking fault thickness, which is two interplanar spacings thick) makes it hard to detect Suzuki segregation experimentally. Nevertheless, the development of Field Emission Gun Transmission Electron Microscopes (FEG TEM) in recent years has largely overcome this difficulty. We have used a FEG TEM to measure the local composition across stacking faults in a Cu-7.15 at% Si alloy annealed at various temperatures. A silicon enrichment, due to the segregation of silicon to stacking faults, was observed at the stacking fault plane and was found to decrease monotonically with increasing annealing temperature. This temperature dependence was used to determine the segregation binding energy, which was thus measured to be -0.021 ± 0.019 eV/atom. This value does not compare favorably with the theoretical estimate calculated from bulk phase diagrams, which overestimates the binding energy.
between resolution and noise. To make the most efficient use of the incident electron dose, we use low-loss spectra where the inelastic scattering cross sections are relatively high. We show that various polymer combinations - aromatic/aliphatic; hydrophobic/hydrophilic - can be differentiated from each other as well as from amorphous ice and frozen organic solvents based on differences in their low-loss spectra. We use these differences to map the distribution of solvents as well as the various polymer components in solvated homopolymer blends for biomaterials applications and ionomer systems for perm-selective membrane applications.

10:15 AM  P6.4  Low Voltage Electron Microscopy of Polymer, Organic Molecular and Biological Materials. Lawrence F. Drummy1, Junyan Yang2 and David Martin2; 1Materials and Manufacturing Directorate, Air Force Research Labs, WPAFB, Ohio; 2Materials Science and Engineering, Macromolecular Science and Engineering, Biomedical Engineering, University of Michigan, Ann Arbor, Michigan.

The application of a table-top sized low voltage electron microscope operating at accelerating voltages near 5 kV to the study of several types of organic materials is presented. The microscope is capable of operating in TEM, STEM, SEM and electron diffraction modes, and it shows extremely high contrast for materials composed of light elements that are notoriously difficult to image in traditional high voltage instruments. Data from a wide range of samples will be presented, including films of the octapentacene, multi-block copolymers, electrospray nanofibers, biological microtubes and biopolymer thin films. A detailed description of electron as a tool to image these films at 5 kV will be given, along with the benefits and limitations of the use of an in-house computer program for the compilation of the electron beam stability of several crystalline polymers as a function of incident electron energy. It was found that this variation in beam stability as a function of energy can be reasonably well represented by the expected variation in cross section for carbon k-shell ionization. The carbon cross section is highest at voltages near 5 kV, giving such high contrast at this voltage that the need for staining samples can be significantly reduced or eliminated altogether. Furthermore, multi-slice calculations of microtubes also showed significantly more image contrast at 5kV than at 400 kV.

10:30 AM  P6.5  Synthesis and Microstructures of α-Fe2O3 Bicrystalline Nanowires. Rongming Wang1, Yunyi Fu2, Han Zhang1 and Christian Kisielowski2; 1State Key Laboratory for Mesoscopic Physics, School of Physics, Peking University, Beijing, China; 2National Center for Electron Microscopy, Lawrence Berkeley National Laboratory, Berkeley, California.

Novel millimeter-area nanowires of Fe2O3 have been successfully synthesized by a simple oxidation process of pure iron. The microstructure of the Fe2O3 nanowires have been systematically investigated by means of X-ray diffraction, scanning electron microscopy, transmission electron microscopy (TEM). The investigated materials are found to be stoichiometric rhombohedral α-Fe2O3 with the side length of a few micrometers to tens of micrometers. Besides the single crystal Fe2O3 nanowires, a great amount of bicrystalline nanowires can also be found with ellipsoidal ends. Investigations indicate that most of the bicrystalline nanowires are nano-twins and their orientation relationship is 〈111〉M/〈110〉T, [110]M/[100]T or [110]M/[101]T. High resolution TEM with numerical reconstruction procedures have also been used to investigated the atomic structure of the micro-twins and the model for the interface has also established. The growth mechanisms of such interesting and unique nanostructures are briefly discussed on the base of oxidation process. Thanks for the National Key 973 projects (MOST, No. 2002CB613605) and NSFC (No. 10374003) for financial support. RM Wang acknowledges the support from the Berkeley Scholar Program.

10:45 AM  P6.6  Microscopy study of Molybdenum Sulfide Nanoribbons. Alejandro Camacho-Bragado1, Jorge A. Ascencio2 and Miguel Jose Yacaman3,4,5,6; 1Texas Materials Institute, University of Texas Austin, Austin, Texas; 2Programa de Investigacion y Desarrollo de Dictos, Instituto Nacional del Petroleo, Mexico City, Mexico City, Mexico; 3Chemical Engineering, University of Texas Austin, Austin, Texas; 4Chemistry, University of Illinois at Urbana-Champaign, Urbana, Illinois; 5Physics, Yeshiva University, New York, New York; 6Materials Science & Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois; 7Civil and Environmental Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois.

There were synthesized very large films of self-assembled molybdenum sulfide nanoribbons. Molybdenum sulfide nanoribbons and fullerenes have been systematically studied, however some other nanostructures are yet to be explored. It is expected that open structures such as ribbons and wires show rather different properties than nanotubes. Similarly to nanotubes these structures will show strong quantum confinement in two dimensions, but having open structure they are expected to remain active to HDS reactions as well as to some other redox reactions. Large amounts of molybdenum sulfide nanoribbons have been prepared by a two-step process, first molybdenum oxide nanostructures are prepared by hydrothermal reactions in acidic medium. Second, the self-assembled film is sulfidized. The initial morphology is retained and different stoichiometries can be obtained. The width of these nanoribbons ranges between 150 and 300 nm depending on the synthesis conditions. The result materials have been studied by electron microscopy techniques. Electron energy loss spectroscopy has shown the complete substitution of oxygen by sulfur. Nanobeam diffraction has been used to determine the structure, orientation and growth direction of these ribbons. High Angle Annular Dark Field together with bright field images show sulfur rich areas, whose role in catalytic processes are yet to be determined.

11:00 AM  P6.7  Development of Nano-Bimetallic Catalysts for the Removal of Nitrate from Drinking Water. Huiping Xu1, Kathryn Guy2, John Shapley3, Anatoly Frenkel3, Duane Johnson3, Charles J. Werth2 and Judith C. Yang1; 1Materials Science & Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania; 2Chemistry, University of Illinois at Urbana-Champaign, Urbana, Illinois; 3Physics, Yeshiva University, New York, New York; 4Materials Science & Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois; 5Civil and Environmental Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois.

Reductive removal by hydrogenation using supported Pd/M bimetallic metallic catalysts has emerged as a promising alternative for the removal of many water contaminants including nitrate [1]. However, the bimetallic catalysts (Pd/M)Al2O3 currently available are not sufficiently selective for nitrate removal, because of the high selectivity of the bimetallic catalysts for the reduction of water to hydrogen. On the other hand, the reduction of nitrate is also significantly higher than permitted levels. We hypothesize that different Pd/M (M=Ca, Sr, Mn, Co, Fe, Mo, Ni, Rh, Ir, Mn and Cr) combinations on unique support structures can yield significant improvements in nitrate reduction rates and dinitrogen selectivity. In this work, we only focus on PVP stabilized nanoscale Pd/Cu colloids with metal ratios ranging from 50:50 to 90:10 (Pd/Cu) and present their synthesis, structure and selectivity/activity, with particular emphasis on the structural characterization by both ex situ and in situ electron microscopy and synchrotron x-ray spectroscopy. In order to evaluate the particle size and understand their morphology, we used a dedicated scanning transmission electron microscopy (STEM) (probe size 0.5nm). The key point with high angle (~60mrad) annular dark-field imaging is that the intensity of the (K-Rutherford) scattered beams is predominantly incoherent [2] and depends on the Z, atomic number. Thus, heavy atoms (such as Pd and Cu) stand out very clearly on a light background of C and O. Analysis by energy dispersive X-ray emission (EDX) further confirmed the relative average atomic proportions of the bimetallic particles. Synchrotron x-ray spectroscopy (EXAFS and NEXAFS) further examines the uniformity of the supported bimetallic nanoparticles. Electron diffraction and high resolution electron microscopy (HREM) will be used to determine the crystallinity and crystal structure of individual bimetallic particles. Nuclear Magnetic Resonance spectroscopy and Fourier Transform Infrared Spectroscopy will be used to monitor in situ nitrate reduction and further probe the reaction mechanisms on the catalyst surface. Our studies of PVP stabilized Pd50Cu50 colloid show that the particles are uniformly bimetallic PdCu alloy with FCC structure, average size of 3.3 nm and narrow distributions. This approach will allow us to probe the relationship among nitrate reactivity/dinitrogen selectivity, Pd/Cu amounts, mass transfer limitations and structure at the nanoscale, essential for the efficient development of catalysts for the purification of drinking water. [1]. A. Kapoor and T. Variraghavan, J. of Environmental Engineering, 123, 371 (1997). [2]. A. Singhal, J.C. Yang and J.M. Gibson, Ultramicroscopy, 67, 191 (1997). Supported by the University of Pittsburgh, School of Engineering Heinz and Bevier endowments.

11:15 AM  P6.8  Crystallization of Silver Stearate from Sodium Stearate Dispersions. Jingshun Dong1, David Whitcomb2, Bin Lin1, Alon McCormick1 and Howard Ted Davis1; 1Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota; 2Eastman Kodak Company, St. Paul, Minnesota.

Silver carboxylates, the common silver source used for photothermographic imaging materials, are normally obtained from the reaction between sodium stearate and silver nitrate. Crystals are formed together with the on-grid reaction technique, directly images silver stearate microstructures at the initial stages of silver stearate precipitation, within the first 30 seconds. The silver stearate reaction product first forms particles about 5 nm in size, which is similar to the ds-spacing of the final crystals. These particles aggregate to produce larger and loosely packed embryonic crystals, the precursors to the ultimate silver stearate crystals.
Dispersion of gold nanoclusters in single crystal TiO2, MgO, and SrTiO3 has been found to influence the optical properties of the dielectrics. One speculative explanation to this is the formation of quantum antidots (nanometer-sized vacancy clusters), which are believed to be spatially located at the interface between the Au clusters and the matrix. To verify this proposition, Au nanoclusters dispersed in TiO2, MgO, and SrTiO3 were prepared by ion implantation at 300 K and 975 K and subsequent annealing at 1275 K for 10 hours. High resolution transmission electron microscopy and high-angle-annular-dark-field (HAADF) imaging in an aberration corrected scanning transmission electron microscope (STEM) have been used to characterize the microstructure of the gold nanoclusters dispersed materials. STEM-HAADF imaging is a powerful method for direct imaging of the Au atoms and cavity cluster distributions. The results indicate that Au atoms substitute for cations in these systems. Cavities of up to several tens of nanometers are observed in TiO2 and SrTiO3. The nanometer-sized cavities and the Au cluster are faceted along the same lattice plane of the matrix, indicating that the interfacial energy defined by Au clusters and matrix follows the same order of the surface energy for different lattice planes. The Au clusters and the cavities show spatial association, indicating a strong interaction during their respective clustering process.

11:45 AM P6.10

In this work we carried out the chemistry and structural analysis of the Central Dark Line of the human tooth enamel by High Resolution Electron Microscopy techniques such as Angle-resolved Energy Loss Spectroscopy (EELS), Electron Dispersion Spectroscopy (EDS), Z-Contrast, and Nanodiffraction, with the aim of finding the differences, if there is one, between Hydroxyapatite and the Central Dark Line. The result indicated any difference in the chemical composition of the Central Dark Line and the remainder of the crystal. On the other hand, the Z-Contrast and Nanodiffraction were the most indicated techniques for this study. Another technique we used too much in this study was the Digital Image Processing to enhance the Central Dark Line contrast and detect some differences among the periodicities of the planes of the enamel crystals parallel to the Central Dark Line. These differences give some idea on a different material for the Central Dark: instead of Hydroxyapatite, it could be composed by another Calcium Phosphate phase, such as Octacalcium Phosphate (OCP). We thank the technical help from P. Mexia, L. Rendon, R. Hernandez, M. Aguilar, S. Tosucucano, C. Flores, C. Maguna, C. Zorrilla, and A. Sanchez. This work was economically supported by DGAPA-UNAM with the project IN-104992.

SESSION P7: In-situ Microscopy of Deformation and Growth (Even in Liquids)
Chair: Jeff De Hosson and Eric Stach
Wednesday Afternoon, December 1, 2004
Gardner (Sheraton)

1:30 PM *P7.1
Electron Microscopy of the Operation of Nanoscale Devices. John Paul Cummings1, David Goldhaber-Gordon2, A. Zettl2, M. R. McCartney3 and J. C. H. Spence4; 1Department of Physics, Stanford University, Stanford, California; 2Department of Physics, University of California, Berkeley; 3Materials Sciences Division, Lawrence Berkeley National Lab, Berkeley, California; 4Center for Solid State Science, Arizona State University, Tempe, Arizona; 5Department of Physics and Astronomy, Arizona State University, Tempe, Arizona.

A transmission electron microscope (TEM) is much more than just a tool for imaging the static state of materials. With the relevant length scales of both the devices reaching into the nanometer-domain, TEM is also emerging as a powerful tool for studying the dynamic properties of these new functional devices. It is straightforward to study real-time device failure, but it is also possible to use an electron microscope to uncover subtle effects of device operation, such as structural changes, mass transport, electromagnetic fields, and heat flow. I will outline the general techniques in making this sort of in-situ microscopy possible. Specifically, I will present work on studying the mechanical and electrical properties of carbon nanotube devices. Multiwall carbon nanotubes are commonly packed tubular networks with a spacing between each cylinder is simply the natural spacing of graphite. Using a custom-built in-situ nanomanipulation probe, we have shown that it is possible to slide the nanotube layers in a telescopic extension mode that exhibits low friction, demonstrating the potential of nanotubes as the ultimate synthetic nanobearing. During this telescopic extension, the electrical resistance of the nanotube devices increases, opening the possibility that these devices can also be used as nanoscale rheostats. I will also present work on using electron holography in a TEM to study the electric field distribution in nanotube field-emission devices and on using a nanotube itself as a biprism for electron holography. These measurements together demonstrate the wealth of information that can be obtained and frontiers that can be opened by putting operational nanodevices inside an electron microscope.

2:00 PM P7.2
Formation and Manipulation of a Gold Nanowire and a Gold Nanocrystal by using a STM Probe inside a HRTEM. Jianyu Huang, Shuo Chen and Zhifeng Ren; Boston College, Chestnut Hill, Massachusetts.

We produced a gold nanowire with diameter of about 10 nm and length of about 15 nm by pulling a gold contact formed by contacting two scanning tunneling microscopy (STM) probes inside a high resolution transmission electron microscope (HRTEM). The gold nanowire was later subjected to large compression deformation between the same two STM probes, where the gold nanowire reduced its length while expanded its diameter to accommodate the deformation. The nanowire was eventually flattened to fill the gap between the two STM probes. At the final stage of compression, a gold nanocrystal of about 5 nm in diameter was generated directly from one end of the nanowire, possibly caused by dynamic recrystallization. This gold nanocrystal was further compressed by the same STM probe, and it was found that twinning was the dominant deformation mode during the compression. The results provide new insight into the formation mechanisms and deformation behavior of low dimensional materials, such as nanowires and nanocrystals.

2:15 PM P7.3
Dynamic observations of electrochemical nucleation and growth phenomena in the transmission electron microscope. Frances M. Ross1, A. Radicio2, P. C. Scarson2, M. C. Reuter3, J. B. Hannon1, S. J. Chey1 and P. M. Vereecken1; 1IBM TJ Watson Research Center, Yorktown Heights, New York; 2Department of Materials Science and Engineering, The Johns Hopkins University, Baltimore, Maryland.

Nucleation and growth phenomena which take place from the vapour phase, for example during thin film formation by chemical vapour deposition, have been studied extensively in situ in the TEM using environmental cells or differential pumping. The real-time kinetic data which has been obtained has been valuable in providing detailed information about the control vapour phase growth. However, many industrially important processes, such as electrochemical deposition, occur from the liquid rather than the vapour phase, and have so far been less accessible to in situ imaging and analysis. In this presentation we will therefore describe the design, construction and operation of a liquid cell for the study of electrochemical and other liquid phase reactions in the TEM. The cell is based on the use of silicon nitride membranes to confine the liquid to an electron transparent layer. Electrodes are patterned within the cell allowing deposition to be observed in real time under control of a potential potentiostat. We will show simultaneous electrochemical and video-rate microstructural measurements of the nucleation and growth of copper clusters from oxidised copper sulphate solution. Measurements of cluster growth kinetics clearly resolve the two expected limiting growth regimes, where cluster growth is controlled either by the rate of copper ions through the liquid (at high growth rates) or by the rate of the reaction on the cluster surface (at lower growth rates). However, these measurements also show that a simple model of nucleation and direct attachment is inadequate to account for the observed growth rate of individual clusters. We will therefore describe an alternative scenario where the initial stages of nucleation and growth are strongly influenced by surface diffusion on the electrode. We will then discuss the effects of ion concentration and additives on the morphology of the nuclei, where microstructural and kinetic measurements reflect the different importance of surface and liquid processes. We will finally consider how this cell may be used to observe other liquid phase phenomena in the TEM.
This paper presents challenges and opportunities to control the microstructure in nano-structured metal systems via a relatively new approach, i.e., using a so-called nanocluster source. An important aspect is that the cluster size distribution is monodisperse and that the kinetic energy of clusters during deposition is very low. Interestingly the clusters are grown in extreme non-equilibrium conditions, which allow obtaining metastable structures of metals and alloys. The combination of factors such as temperature, kinetics, impurities, and strain energy effects could lead to unusual nanoparticle shapes and size distributions. Therefore, it is crucial to study these controlling factors in detail with high-resolution transmission electron microscopy. In this contribution we show the excellent coherence of cluster deposition to the basic building block of Fe, Nb, Mo and Co, i.e. the structure and properties of a single cluster studied with high-resolution transmission electron microscopy, followed by an in-situ TEM study of the coalescence and diffusion of clusters (sizes ranging between 3 nm and 10 nm) leading to the growth of nano-structured metal films. Clusters were deposited directly on Si/SiN and carbon support films of thickness 20 nm for TEM analysis. Growth front aspects of Cu nanocluster films deposited with low energy onto silicon substrates at room temperature have been investigated by atomic force microscopy (AFM). Annelling of clusters, which are in contact, leads to their fusion and formation of larger clusters preserving their crystallographic structure and being free of any strain. However, during coalescence the clusters of similar size rearrange themselves in an arch shape area where a finite size neck is formed leading thereby to full coalescence. This observation is in contrast with theoretical descriptions of coalescence assuming initially a point contact as a pathway to coalescence.

Effect of Sn Roughening Transition Temperature of the Interface between Liquid Pb and Solid Al. Liu Xia Zhang1, Erik Johnson2 and Uli Dahmen1; 1National Center for Electron Microscopy, Lawrence Berkeley National Laboratory, Berkeley, California; 2Nano Science Center, Niels Bohr Institute, University of Copenhagen, Department of Materials Research, RISO National Laboratory, Copenhagen, California.

Cuboctahedral inclusions embedded in an Al matrix show an interesting shape change during isothermal annealing after melting. The (100) truncations of the inclusions become rounded caps immediately after melting while the (111) planes remain faceted until a critical transition temperature is reached. As a result of a kinetic limitation, the shapes of liquid inclusions depend on size and temperature. When the inclusions melt, smaller particles round off quickly, but larger particles remained faceted indefinitely. From kinetic observations on the rounding of inclusions as a function of size, it is possible to determine an interface roughening temperature corresponding to disappearance of the ledge nucleation energy. Above the roughening transition temperature, interfaces are atomically rough and can advance without the need for ledge nucleation. In all inclusions, the smallest size clusters rearrange themselves in an arch shape where a finite size neck is formed leading thereby to full coalescence. This observation is in contrast with theoretical descriptions of coalescence assuming initially a point contact as a pathway to coalescence.

Formation and Growth of Epitaxial Cobalt Germiane Co5Ge7 Films Studied by In-situ Ultrahigh Vacuum Transmission Electron Microscopy. Xiaoping Pan1, Haiping Sun1, Yanbin Chen1, Dongchi Chi2, Ramesh Nath2 and Yong Lim Foo2; 1University of Michigan, Ann Arbor, Michigan; 2Institute of Materials Research and Engineering, Singapore, Singapore.

Si-based transistor technology is approaching its limit to achieve enhanced transistor speed and reduced power consumption for next generation CMOS applications. Ge is recently considered as an alternative to Si by semiconductor industry to meet the sub-45 nm technology requirements due to its high carrier mobility and excellent compatibility with high-k materials. Metal germicides will be used as contact materials in the future Ge-based device. Compared with silicones that have been extensively investigated in the past, research on the formation of germicides on single crystal Ge surface attracted less attention. In this work, we report the formation of epitaxial Co5Ge7 on a single crystal Ge (001) surface by both solid state reaction, i.e. deposit Co on Ge surface at room temperature followed by annealing at high temperatures, and reactive deposition, i.e. the Ge substrate was maintained at elevated temperature during deposition to ensure immediate phase formation. The Ge substrate was deposited by sputter deposition at high rate (4 Å/s) and composition (Ge, Co) characterized by XPS. This work was carried out within a transmission electron microscope modified for in-situ deposition of materials under ultra high vacuum. Atomic Co flux was generated by electron beam evaporation of a high purity Co rod from an evaporator attached to the microscope. The formation and evolution of epitaxial Co5Ge7 islands during the reaction of Co with Ge were directly observed during the reaction/deposition. We have found that the formation and growth of the Co5Ge7 phase involves different mechanisms as the two experiments mentioned. The identification of the Co5Ge7 phase by electron diffraction analysis will be discussed in detail.
Investigation of metals and their alloy oxidation during initial stage (or nano-oxidation stage) is essential to improve passivation properties of corrosion-resistant coatings or self-assemble of nano-oxide structure for functional devices. Nevertheless, limited accessibility to oxide structure evolution by traditional methods has restricted our understanding of kinetics of nano-oxidation. By using in situ ultra-high vacuum (UHV) transmission electron microscopy (TEM) with variable temperature and gas pressure, quantitative data regarding structural evolution and kinetic processes of metal oxidation can be visualized. Previous investigations have focused on Cu single crystal and heteroepitaxial concepts were successfully used to describe nano-oxidation. In the present work we extend our knowledge to alloy oxidation by studying Cu-Au alloy nano-oxidation. Here Cu-Au is selected because Au is a noble element which does not form stable oxide at the experimental conditions and Au forms a continuous solid solution at the temperature and composition that we investigated, so that the results can be readily compared with Cu nano-oxidation. The oxidation of Cu50at%Au (Cu0.5Au0.5) was studied by in situ UHV-TEM at 550°C to 700°C and oxygen partial pressure of 5×10^-4 torr. For all temperatures investigated, square-shaped Cu2O islands grow with cube-on-cube crystallographical orientation to the Cu-Au film. This is attributed to greatly reduced strain energy in Cu2O/Cu0.5Au0.5 system. For the growth kinetics, initially cross-section area of the islands scales with time linearly which suggests an oxygen surface diffusion dominated 3D island growth mechanism. As the islands grow, Au is partitioned out from the growing interface and enriches around the island as Au concentration increases, it retards the growth. Finally, the oxide islands stop growing and a self-limiting behavior results. In the later stage of growth, Au diffuses away or Cu diffuses to the growing front is rate-limiting mechanism. EDS (energy dispersive spectrum) elemental mapping and line scan as well as STEM (scanning transmission electron microscopy) images confirm Au enrichment around islands.

Recently, heteroepitaxial self-assembled quantum dots (QDs) can be grown in the Stranski-Krastanow (S-K) mode and considerable effort has been devoted to fabricate laser devices, photodetectors and advanced memories by using self-assembled QDs. For improved control of the microstructures of QDs, it is necessarily required that effects of process parameter on the growth characteristics of QDs should be quantitatively understood. In particular, growth temperature and thermal stability are important because the temperature dependent surface diffusion of the adatoms affects the structural and optical properties of the QDs. In the present study, the thermal stability of self-assembled InAs QDs grown on GaAs(001) substrate has been investigated by in situ high resolution transmission electron microscopy. Molecular beam epitaxy was employed to grow QDs and the structure and thermal stability of QDs were investigated by using a 200 kV FEG-TEM (JEM2010F) and a 1250 kV high-voltage TEM (The Morning Star, KBSI). The uncapped QDs exhibited dome-shape structure in the early stage of growth. However, after capping with GaAs, they were changed into flat-pyramidal shape with the height of 5-8 nm and the lateral width of 15-25 nm along [-110] direction. As the analyzed temperature increased, the QD structure remains stable up to 550°C. However, higher temperature results in the decrease of the QD height and the QD density decreased abruptly above 600°C. During the observation in a high-voltage electron microscope at high temperature, irradiation defects, such as twin, stacking fault and amorphization, were also generated in near surface regions.