

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

9:00 AM *P1.1

Imaging Single Atoms with Z-contrast STEM: Current Results and Future Prospects. Paul Voyles¹, David A. Muller² and John Grazul²; ¹Materials Science and Engineering, University of Wisconsin-Madison, Madison, Wisconsin; ²Applied and Engineering Physics, Cornell University, Ithaca, New York.

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 Sb atoms in Si revealed that the defect responsible for rendering these dopants electrically inactive must contain two Sb atoms. The details of the Sb 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 Sb 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 enable useful 3D imaging by optical sectioning. The current generation C_s 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 can dominate optical defocus 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] N. Delby et al., *J. Elec. Mic.* 50, 177 (2001). PMV acknowledges support from the UW NSF MRSEC on Nanostructured Materials and Interfaces (NSF DMR-0079983).

9:30 AM P1.2

Studies of Nanocatalysts with Single-Atom Sensitivity. Albina Borisevich¹, Sanwu Wang², Sergey N. Rashkeev², Andrew R. Lupini¹, Karl Sohlberg³, Sokrates T. Pantelides^{2,1} and Stephen J. Pennycook^{1,2}; ¹ORNL, Oak Ridge, Tennessee; ²Vanderbilt University, Nashville, Tennessee; ³Drexel University, Philadelphia, Pennsylvania.

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 kV VG Microscopes¹ HB603U STEM with Nion aberration corrector has a demonstrated resolution of 0.61 angstroms and routinely allows imaging of single atoms inside materials and on their surfaces. Such observations also provide a direct link to first-principles calculations thus facilitating the solution of complex materials problems. In particular, aberration corrected STEM is a powerful tool for the studies of heterogeneous catalysts, where it becomes possible to connect the structure of metal clusters on the oxide support with the macroscopic properties of the system. In the studies of La-doped γ -Al₂O₃ catalytic supports, the single-atom imaging and theoretical calculations allowed identification of isolated La atoms adsorbed on γ -Al₂O₃ surface as the instruments of the dopant-induced thermal stabilization [1]. In a related system, accurate measurements of the interatomic distances of the Pt₃ clusters on the surface of γ -Al₂O₃ and thorough theoretical analysis led us to discover that these units are capped with OH-groups, which affect electron density distribution within the clusters and, consequently, the catalytic activity of the system. Improved signal-to noise ratio of the aberration-corrected microscope allows visualization of the substrate and dopant structure simultaneously, providing more details on their interaction, as we were able to demonstrate for Cr₂O₃- γ -Al₂O₃ and other cases. In the catalytic systems where several metals are involved, Z-contrast imaging can provide atom-by-atom identification and thus distinguish bimetallic and segregated particles. Most importantly, the high convergence angle of the probe in aberration-corrected HAADF STEM results in depth sensitivity, enabling vertical resolution in the nanometer range in addition to sub-angstrom lateral resolution. Focal series of the STEM images can thus be used for determination of the three-dimensional structure of mesoporous or polycrystalline substrates and characterization of the vertical distribution of the catalytic particles. It was demonstrated effective for the systems such as (Pt, Ru)/ γ -Al₂O₃ and (Pt, Au)/anatase, where the vertical location of single atoms and nanometer-size particles with respect to the substrate was determined. Work is currently underway to establish the best conditions for a similar observation of a single atom within a crystal. Prospects for in-situ aberration-corrected HAADF STEM in ORNL will also be discussed. [1] S. Wang, A. Y. Borisevich et al., *Nature Materials* 3, 143 (2004).

9:45 AM P1.3

3D Location of Single Hf Atoms at a Si/SiO₂/HfO₂/p-Si Gate Dielectric. Klaus van Benthem¹, M. Y. Kim² and S. J. Pennycook¹; ¹Oak Ridge National Laboratory, Oak Ridge, Tennessee; ²Samsung Advanced Institute of Science and Technology, Suwon, South Korea.

The three-dimensional location of single atoms has recently been addressed to be the main issue for controlling properties and life-times of semi-conductor devices (for instance field-effect transistors) due to a segregation or pinning of dopant atoms at the Si/dielectric 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 for recording high-angle annular dark-field images in a VG HB603 U dedicated 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 deconvolution of the recorded image stacks with a three-dimensional point-spread function, were used to enhance the accuracy in determining the vertical atom positions. As a result, single Hf atoms can be located with an accuracy of 0.61 Angstroms laterally, and better than 1 nm vertically. It was possible to locate single Hf atoms at various depths within the SiO₂ layer of 1 nm thickness, located between the single crystalline silicon substrate and the poly-crystalline HfO₂ film. Reconstructed data sets show that Hf atoms are randomly distributed within the volume of the SiO₂ layer. A preferred segregation of Hf atoms to the Si/SiO₂ surface was not observed. Complementary, atomically resolved electron energy loss spectroscopy allows study of the electronic structure of the interface. Preliminary studies of the Si L_{2,3} and Hf O_{2,3} edges across the interfaces will be shown.

10:30 AM *P1.4

Materials Analysis by Aberration-Corrected STEM. Ondrej L. Krivanek¹, N. D. Dellby¹, M. F. Murfitt¹, Peter D. Nellist¹, Z. Szilagy² and S. J. Pennycook²; ¹Nion Co., Kirkland, Washington; ²Department of Physics, Trinity College Dublin, Dublin, Ireland.

Because of advances made possible by aberration correction, the performance of scanning transmission electron microscopes has recently progressed to a fundamentally new level. Addition of Nion spherical aberration (Cs) correctors to VG STEMs has improved their resolution by 2-2.5x, to <0.1 nm at 100 keV and about 0.06 nm at 300 kV. These levels of performance make single-atom imaging routine, and have already yielded many useful results. At the same time, the current in an atom-sized probe has been increased by 5-10x, up to about 200 pA, resulting in rapid materials analysis by electron energy loss spectroscopy (EELS) and also EDXS, with demonstrated single-atom sensitivity. Aberration correction has also allowed the bright-field collection angle to be increased considerably without a loss of contrast, making the STEM into a reasonably efficient phase-contrast imaging instrument that can routinely detect atomic columns made up of oxygen and other light atoms. The performance of the aberration-corrected STEMs is currently held back by the basic parts of the instruments, whose design dates back to the 70s and 80s for the 100 kV and 300 kV VGs respectively. We are therefore developing a new dedicated STEM column consisting of an ultra-stable cold field-emission gun, a flexible condenser system, a C3/C5 aberration corrector, a flexible objective lens, ultra-stable sample stage, flexible post-sample optics and high-performance EELS. Progress on this system will be described, along with the projected performance and examples of likely future applications.

11:00 AM P1.5

Design and Manipulation of Point Defects at Strontium Titanate Grain Boundaries. Pradyumna Prabhurashi¹, Andrew R. Lupini², Steve Pennycook² and Vinayak Dravid¹; ¹Materials Science and Engineering, Northwestern University, Evanston, Illinois; ²Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Oriented bicrystals of SrTiO₃ are considered as model systems to understand the nonlinear transport, capacitance and space-charge phenomena in oxide electroceramics. Bulk donor (Nb) doped SrTiO₃ bicrystals exhibit non-linear I-V behavior with resistivity almost 4 orders of magnitude higher than their single crystal counterparts. This behavior is attributed to the presence of electrostatic potential barrier at the grain boundaries (GBs). The GB potential barrier can be tailored by oxidation/reduction excursions as well as by GB specific doping with donors and acceptors on appropriate atomic sites of SrTiO₃. The GB barrier tuning occurs as a result of change in the defect chemistry specifically at the interface. By controlling processing

parameters, it is possible to manipulate oxygen vacancy concentration as well as variable valence states exhibited by Mn (as Mn^{2+} and Mn^{3+}) in order to tailor grain boundary barrier characteristics, particularly the barrier height - thus the transport and capacitive properties. The focus of the presentation is to describe the role of advanced electron microscopy to probe the local GB defect phenomena, in order to establish predictive structure-property correlation for GBs. Recent progress in spherical aberration correction for scanning transmission electron microscopy (STEM) now offers the unique opportunity for characterizing the detailed atomic and electronic structure locally at the grain boundary (GB) region, including imaging the elusive oxygen columns at and around the GB core, and high resolution electron energy loss spectroscopy. For example, we observe crystal field splitting between e_g and t_{2g} molecular orbitals of Ti and O is 2.2-2.4 eV for octahedrally co-ordinated Ti-O in bulk $SrTiO_3$. This splitting is reduced locally at the grain boundary by 0.3 eV because of distortion of Ti-O octahedra. Reduction of a $SrTiO_3$ bicrystal at 800 °C in CO/CO_2 atmosphere further distorts Ti-O octahedra locally at the grain boundary resulting in vanishing of the crystal field splitting. Reduction also leads to a 45% increase in Ti/O EEL integrated intensity ratio indicating an increase in oxygen vacancy concentration locally at the grain boundary. Implications of this in terms of the structural changes in Ti-O octahedra and resulting grain boundary barrier properties are being explored using aberration corrected atomic resolution scanning transmission electron microscopy and microscopic electrical transport measurements.

11:15 AM P1.6

Measuring the Interfacial Potential in Tilt 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- T_c 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 cores 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. The cubic perovskite $SrTiO_3$ is regarded as a model system for more complex perovskite oxide grain boundaries. Therefore to develop a fundamental understanding of the structure-property relationships at grain boundaries in perovskites, much can be inferred from the study of the $SrTiO_3$ model system. This study uses an undoped 4° [001] grain boundary in $SrTiO_3$ to measure changes in the atomic structure and composition occurring at the dislocation core. The individual dislocation cores are investigated by atomic resolution Z-contrast imaging and electron energy-loss spectroscopy (EELS) using the 100 keV VG HB501 DSTEM, equipped with objective lens spherical aberration (C_s) corrector. We will show that a probe-size of <0.13 nm (convergence-angle 35 mrad) and energy resolution of <0.4 eV for Z-contrast imaging and EELS can be achieved, allowing column-by-column EELS spectrum imaging with core-loss spectral resolution limited by the life-time broadening rather than the electron beam. The combination of these analytical techniques allows now to study oxygen vacancy concentration, cation non-stoichiometry and Ti valence changes directly as a function of distance from the grain boundary with \AA -accuracy. These measurements show that the electronic properties of grain boundaries are due to Ti-non-stoichiometry and excess of oxygen vacancies that cause a highly doped n-type region in close proximity to the dislocation core. Further, these measurements show the effects of small probe-sizes when positioned between two atomic columns causing dechanneling. These results are used to develop a new model of the grain boundary potential in $SrTiO_3$. This work was supported by the Division of Materials Sciences, U.S. Department of Energy, under Contract No. DE-AC02-98CH10886.

11:30 AM P1.7

Simultaneous Z-Contrast and Phase Contrast Imaging of Oxygen in Ceramics. Matthew F. Chisholm, Naoya Shibata, Andrew R. Lupini and Stephen J. Pennycook; Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge,

Tennessee.

Many properties of oxide materials are controlled by the presence of crystal defects. Determination of the structure and composition of these defects in oxides is complicated by the difficulty in imaging the oxygen sublattice. Herein, we have examined the oxygen sublattice at $SrTiO_3/Al_2O_3$ interfaces, $SrTiO_3$ grain boundaries and Al_2O_3 dislocations using simultaneous coherent and incoherent imaging techniques. The instrument used in this work is a scanning transmission electron microscope fitted with an aberration corrector. Aberration correction enables smaller, brighter probes with resulting improvements for Z-contrast imaging in resolution, image contrast and signal-to-noise ratio. In addition, via reciprocity, aberration corrected phase contrast images may be obtained simultaneously using a small axial detector. The data show that we can detect oxygen columns in both the Z-contrast and phase contrast modes not only when embedded with relatively light Al columns but also in the presence of Ti and Sr. The Z-contrast technique provides an incoherent image, thus, there is no phase problem for structure determination. The intensity of atom columns reflects their mean square atomic number (Z) and there are no contrast reversals with crystal thickness. In the phase contrast method of high resolution imaging, contrast is sensitively controlled by focus of the objective lens and specimen orientation, thickness and scattering power. This makes the images of unknown structures difficult to directly interpret. However, this sensitivity can be exploited to provide much greater contrast variations than can be obtained from the Z-contrast images of low atomic number elements. The simultaneous Z-contrast/phase contrast image pairs combine the advantages of both techniques and provide improved sensitivity to the oxygen sublattice in ceramic materials. Simulations of both the coherent and incoherent scattering will be used to demonstrate how the defect configurations affect both types of images and will be used to explore the possibility of quantifying oxygen content in the vicinity of defects in ceramic materials.

11:45 AM P1.8

Advanced Transmission Electron Microscopy Studies of the $LaAlO_3/Si$ Interface. Dmitri O. Klenov¹, Darrell Schlom², Li Hao³ and Susanne Stemmer¹; 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, perovskites have the highest k values. The $SrTiO_3/Si$ interface has been extensively characterized. The perovskite $LaAlO_3$ 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) $SrTiO_3$, stoichiometric (001) $LaAlO_3$ surfaces are polar and (001) layers of LaO or AlO_2 stoichiometry carry a formal charge of +1 or -1, respectively. $SrTiO_3/Si$ and $LaAlO_3/Si$ interfaces are thus expected to be fundamentally different. To obtain direct interfaces that allow for a fundamental understanding on the $LaAlO_3/Si$ interface, Si was grown epitaxially on (001) $LaAlO_3$ 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) $LaAlO_3$ 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 more than one low-energy interface configuration. The interface atomic structure is discussed in the context of electrically-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 experimental images are constructed. We show that such electrically favorable (001) $LaAlO_3/Si$ interfaces, developed using simple electron counting arguments, are difficult to realize experimentally.

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

Science. Gianluigi A. Botton^{1,2}, Frans D. Tichelaar² and Guillaume Radtke¹; ¹Materials Science and Engineering, BIMR, McMaster University, Hamilton, Ontario, Canada; ²National Centre for High Resolution Electron Microscopy, Department of Materials Science and Technology, Delft University of Technology, Delft, Netherlands.

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 0.1-0.2eV while maintaining a probe size of approximately 1-2nm. There are also different approaches to achieving a high energy resolution in energy loss spectra using cold-field 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. In this presentation I 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.

2:00 PM P2.2

Advances in Electron Energy Loss Spectroscopy Obtained from Monochromated and/or Aberration Corrected Scanning Transmission Electron Microscopes. Nigel D. Browning^{1,2}, Ilke Arslan³, Andrew L. Bleloch⁴, Rolf Erni¹, Juan Idrobo⁵ and Eric Stach²; ¹Chemical Engineering and Materials Science, University of California, Davis, California; ²National Center for Electron Microscopy, Lawrence Berkeley National Lab, Berkeley, California; ³Materials Science and Metallurgy, University of Cambridge, Cambridge, United Kingdom; ⁴UK SuperSTEM Laboratory, Daresbury Laboratory, Daresbury, United Kingdom; ⁵Physics, University of California, Davis, California.

The recent development of aberration correctors and monochromators for field-emission (scanning) transmission electron microscopes ((S)TEM) 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 (0.01nm) and energy (0.15eV) resolution. While current instrumentation configurations do not permit the optimum 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, while using a cold-field emission Nion Cs-corrected VG microscope, 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 0.4eV 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, nanoprecipitated phases in superconductors and individual dislocations and stacking faults in GaN to highlight the advantages of performing EELS with this level of resolution.

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2:15 PM P2.3

EELS Analysis of Interstellar Dust Particles using a Monochromated Scanning Transmission Electron Microscope. Rolf Erni¹, Nigel D. Browning^{1,2}, Zurong R. Dai³ and John P. Bradley³; ¹Department of Chemical Engineering and Materials Science, UC Davis, Davis, California; ²National Center for Electron Microscopy, Lawrence Berkeley National Laboratory, Berkeley, California; ³Institute for Geophysics and Planetary Physics, Lawrence Livermore National Laboratory, Livermore, California.

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 FeN- sulfides. IDPs are thus unique examples of natural nano-materials of high complexity. The study of the structure and composition of IDPs, e.g. oxidation states of inclusions, analysis 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 F20 UT scanning 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 Hopfield 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 mode is indispensable. Due to the beam sensitivity of the porous particles, the gas contained in the bubbles could be released after longer exposure times (> 1 min). This effect made it possible to unambiguously 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 (530.5 eV) from the pre-peak observed for Fe-oxide inclusions (2.2 eV width at 531.5 eV). The oxidation state of Fe (2.6-2.7) in Fe-oxide particles measured by the L3/L2 white-line intensity ratio (second derivative method) reveals a dominance of magnetite Fe₃O₄.

2:30 PM P2.4

Energy Filtering TEM on TiAlOx Alloy Oxide for New Generation of CMOS Gate Dielectric with Sub-Nanometer Resolution. Bernd Kabius¹, Nestor Zaluzec¹, Crispin J.D. Hetherington², Angus Kirkland², Jon Hiller¹, Wei Fan¹, Sanjib Saha¹, Orlando Auciello¹ and John A. Carlisle¹; ¹MSD, Argonne National Laboratory, Argonne, Illinois; ²Department of Materials, University of Oxford, Oxford, United Kingdom.

Ultra thin films of TiAlO_x alloy oxide on silicon have a high potential for replacing SiO₂ as the gate oxide in MOSFET devices with structure widths below 100 nm. Al₂O₃ and TiO₂ have a potential for creating a hybrid structure with high dielectric constant and low tunneling current for the next generation MOSFET devices. We developed a room temperature oxidation process assisted by atomic oxygen for fabricating thin TiAlO_x-based MOS structures, which exhibit high capacitance density (EOT = 0.4-0.5 nm) and a leakage which is four decades lower than that of SiO₂. Important parameters for the characterization of these oxide layers are barrier width and chemical concentration gradients. The analysis of interfacial SiO₂ which can have a thickness below one nanometer between gate oxide and Si is also very critical for producing sub-1 nm EOT gate oxides and, therefore, is presenting a significant challenge to electron microscopy. Energy filtering transmission electron microscopy (EFTEM) has already been demonstrated to allow element mapping with high spatial resolution and appears to be suitable for these measurements because several artifacts known from other high-resolution methods, e.g. contrast delocalization, do not hamper the interpretation of EFTEM results. Furthermore, radiation damage and contamination are less severe as compared to focused electron beam methods. The major electron optical parameters influencing spatial resolution of elemental maps obtained by EFTEM are chromatic aberration (Cc), energy width and beam convergence. Present instrumentation without aberration correction allows at an acceleration voltage of 200kV a resolution of about 0.5 nm. Concentration profiles of Al, Si, Ti and O were calculated from energy filtered images of a cross-sectional sample obtained with an uncorrected microscope (Cs = Cc = 1.2mm). A layer containing a high concentration of Al and O with a thickness of approximately one nanometer between the substrate Si and a 3 nm thick TiAl-oxide layer could be detected. Correction of spherical aberration Cs improves the resolution theoretically to about 0.3nm because beam convergence does not influence the resolution if Cs is zero. The Cs corrected microscope in Oxford has been used to demonstrate the enhanced EFTEM capabilities. Further improvement can be expected from Cc correction. For very small values of Cc the influence of the width of the energy selection aperture on resolution can be neglected. This will allow atomic level element mapping in the future even for elements with transitions at high energy loss. The submitted manuscript has been created by the University of Chicago as Operator of Argonne National Laboratory under Contract No. W-31-109-ENG-38 with the U.S. Department of Energy.

2:45 PM P2.5

200kV Analytical Electron Microscope With A Monochromator. Masaki Mukai¹, Toshikatsu Kaneyama¹, Takeshi Tomita¹, Katsushige Tsuno¹, Masami Terauchi², Kenji Tsuda², Mikio

Naruse¹, Toshikazu Honda¹ and Michiyoshi Tanaka²; ¹JEOL Ltd., Akishima, Tokyo, Japan; ²Tohoku University, Sendai, Miyagi, Japan.

We have been developing a 200kV analytical electron microscope, which is equipped with an Wien-filter monochromator and an Ω -filter analyzer^{1,2}. The target performance of the microscope is to achieve an energy resolution of 0.2eV with a smaller than 2nm diameter probe on a specimen plane. The monochromator is located between the extraction anode of a ZrO/W emitter and the accelerating tube. The monochromator consists of two octopole-type Wien-filters³ and a slit for energy selection. The lengths of the upper and lower filters along the optical axis are 40mm and 10mm, respectively. A wedge-shaped slit is set between the two filters. This configuration of the two Wien-filters and the slit should produce a monochromatic, achromatic and stigmatic electron beam on the specimen plane. When the monochromator is turned on, the presently ultimate energy resolution is 0.14eV at a 50msec. exposure. An energy resolution better than 0.2eV has been achieved for an exposure time shorter than 10 seconds. When the monochromator is turned off, the energy resolution is 0.55eV, which is almost the ideal value of the ZrO/W emitter. The oval shaped beam is obtained on the specimen plane at 0.14eV energy resolution. The direction of the longer axis of the electron beam corresponds to the energy dispersion of the monochromator. The oval shape of the beam implies that the imperfect achromatic beam on the specimen plane is obtained, which may be caused by the imperfect electron trajectories inside the monochromator. To achieve an achromatic and stigmatic beam smaller than a 2nm diameter on the specimen plane, we have started to manufacture a new monochromator⁴. The new monochromator consists of two dodecapole-type Wien-filters and a parallel shaped slit for energy selection. The width of the slit is selectable. With the new monochromator, we would obtain a better achromatic and stigmatic beam on the specimen plane with a better energy resolution and a more beam current. References 1. M. Tanaka et al.: Inst. Phys. Conf. Ser., **165**, 217-218 (2000). 2. M. Mukai et al.: Microsc. Microanal., **9** (Suppl. 2), 954-955 (2003). 3. M. Terauchi, M. Tanaka, K. Tsuno and M. Ishida: J. Microscopy, **194**, 203-209 (1999). 4. K. Tsuno, D. Ioanovicu, G. Martinez: Microsc. Microanal., **9** (Suppl. 2), 944-945 (2003).

3:30 PM P2.6

Spatially Resolved Valence Determination in Rare Earth and Transition Metal Oxides by Electron Energy-Loss Near-Edge Structure. James Bentley¹, Shelley R. Gilliss², C. Barry Carter²,

Paul G. Kotula³ and Ian M. Anderson¹; ¹Metals & Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; ²Chem Eng & Mat Sci, University of Minnesota, Minneapolis, Minnesota; ³Materials Characterization Dept, Sandia National Laboratories, Albuquerque, New Mexico.

The L_3/L_2 white-line intensity ratio for the 3d transition metals and the M_5/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 CeO₂) abrasives used for chemical-mechanical polishing (CMP), electron energy-loss spectrometry (EELS) measurements recorded as spectrum lines in STEM mode have revealed that the surfaces of the nano-scale particles are reduced through the segregation of trivalent impurities such as La, 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_5/M_4 white-line intensity ratio from Ce⁴⁺ to Ce³⁺ 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 published x-ray absorption spectra of ceria in various oxidation states. Spectrum lines of Co L_{23} and oxygen ELNES have been recorded in the TEM mode at a resolution of 1 nm across cobalt oxide periclase (CoO) - spinel (Co₃O₄) interfaces with the use of an area-selecting slit in a Gatan image filter (GIF). The increase in L_3/L_2 white-line intensity ratio in going from the mixed Co³⁺ and Co²⁺ of the spinel structure to the Co²⁺ of the periclase structure is accompanied by a binding energy reduction of 1.5 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_{23} ELNES by multivariate statistical analysis reveals an interface spectrum that is not modeled well by a linear combination of spectra from CoO and Co₃O₄. 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 SHaRE 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.

3:45 PM P2.7

Surface Chemistry of Combustion-Synthesized Iron Oxide Nanoparticles Determined by Energy Filtered Transmission Electron Microscopy. Valerie J. Leppert¹, Kent Pinkerton² and

Jacek Jasinski¹; ¹Engineering, UC Merced, Merced, California; ²Center for Health and the Environment, University of California, Davis, California.

Iron and soot are common environmental contaminants occurring in ultrafine particulate matter in the air. These materials have been experimentally generated, in a manner simulating high-temperature, industrial processes, through the combustion of iron pentacarbonyl in a mixture of acetylene and ethylene. In this case, ethylene was used as the base fuel and acetylene was added in order to control the amount of soot. We found that, under combustion conditions with high amounts of acetylene, the surface chemistry of iron oxide nanoparticles generated in the flame was consistently different from that of their interiors. Specifically, Energy Filtered Transmission Electron Microscopy (EFTEM) was used to collect Fe $L_3:L_2$ white line-intensity ratio maps of the iron oxide nanoparticles. This ratio is sensitive to any change in the iron oxidation state, and indicated that iron oxide nanoparticles co-generated with soot during combustion processes show a subsurface layer (of thickness 2-3 nm) of decreased iron oxidation state. This observation was confirmed by nanoprobe electron energy-loss spectroscopy (EELS) studies performed in scanning transmission electron microscopy (STEM) mode. A quantitative analysis of the iron L-edge measured in nanoprobe mode indicated that in particles co-generated with soot, the oxidation state of iron at the surface is decreased from Fe³⁺ to Fe²⁺. A comparison of results obtained in EFTEM and STEM mode is made, and correlation of these results with acute respiratory toxicity studies of the laboratory-generated particulate matter is discussed.

4:00 PM P2.8

Characterization of Interface, Composition and Interface in Ti(C_{1-x}N_x)-Ti(C_{1-y}N_y)-Ni Cermets Formed by Liquid Phase Sintering. Seongwon Kim^{1,2}, Jian-Min Zuo¹ and Shinhoo Kang²;

¹The Department of Materials Science and Engineering, UIUC, Urbana, Illinois; ²School of Materials Science and Engineering, Seoul National University, Seoul, South Korea.

Ti(CN)-based cermets have been developed as alternative material to classical WC-Co cemented carbides. They have desirable properties such as high hardness, strength, wear resistance, and high-temperature stability, which are needed for high speed machining. The addition of nitrogen to TiC-based cermets is necessary for these required properties. Ti(CN), the major ingredient of cermets, is the complete solid solution between TiC and TiN, which has the same crystallographic structure and slightly different lattice parameter, depending on nitrogen content. Experiment was carried out in order to examine the relationship between nitrogen content and formation of surrounding structures in Ti(C_{1-x}N_x)-Ti(C_{1-y}N_y)-Ni system during liquid phase sintering. Carbon and nitrogen in the system were illustrated by energy-filtered TEM and local lattice parameters of core and surrounding structure were measured by CBED (convergent beam electron diffraction) technique. It was found that the formation of surrounding structures was facilitated only on Ti(CN) particles with high nitrogen. The variables such as interfacial and strain energy, which determine the formation of surrounding structures, were also examined through the analysis of microstructural development. In this study the role of nitrogen content on the behavior of dissolution and precipitation of Ti(CN) was investigated and explained.

4:15 PM P2.9

Atomic Scale Toughness-Modeling of Silicon Nitride by Rare-Earth Dopants. Alexander Ziegler^{2,3}, Juan Carlos Idrobo¹,

R.L. Satet⁷, M.J. Hoffmann⁷, M.K. Cinibulk⁶, Christian Kieselowski³, Nigel D. Browning^{4,5} and Rob Ritchie^{2,5}; ¹Physics, University of California Davis, Davis, California; ²Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California; ³National Center for Electron Microscopy, Lawrence Berkeley National Laboratory, Berkeley, California; ⁴Chemical Engineering and Materials Science, University of California Davis, Davis, California; ⁵Materials Science and Engineering, University of California Berkeley, Berkeley, California; ⁶Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson Air Force Base, Ohio; ⁷Institut für Keramik im Maschinenbau, Universität Karlsruhe, Karlsruhe, Germany.

Silicon nitride, β -Si₃N₄, ceramics are good candidates for heat-intensive structure applications. Nevertheless, the wide use of the material is limited by its brittleness. The addition of secondary oxide-rare-earth phases to the silicon nitride matrix results in advantages regarding its mechanical properties. However, little is known of how the atomic structure and bonding characteristics of the interface between the intergranular phase and the bulk affect the

mechanical properties of the material. Oxide-rare-earths/ β -Si₃N₄ interfaces were studied by atomic-resolution electron energy loss spectroscopy (EELS) 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 predominately controlled by their atomic radius. In the case of La, which has the largest valence 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 valence shell radius, bond 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 of the valence 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 L₂₃ 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 show worse mechanical 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 the rare-earth dopants at the termination of the open hexagonal Si₃N₄ rings are essential and determinate the mechanical properties of Si₃N₄.

4:30 PM P2.10

High-Resolution Interface Atomic Structure Analysis in Silicon Nitride Ceramics. Alexander Ziegler^{1,2}, Juan C. Idrobo³, Raphaele L. Satet⁴, Michael J. Hoffmann⁴, Michael K. Cinibulk⁵, Christian Kisielowski⁶, Nigel D. Browning^{2,6} and Robert O. Ritchie^{1,7}. ¹Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California; ²Department of Chemical Engineering and Materials Science, University of California, Davis, California; ³Physics Department, University of California, Davis, California; ⁴IKM, University of Karlsruhe, Karlsruhe, Germany; ⁵Materials and Manufacturing 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, Berkeley, California.

Silicon nitride ceramics consist of elongated Si₃N₄ matrix-grains that are randomly oriented and interlocked, and mostly interspersed with a 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, atomic structure 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 because it was impossible to assess detailed information 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 between Si₃N₄ matrix grains and the intergranular phase in silicon nitride ceramics doped with La, Sm, Er, Yb and Lu. Using high-resolution STEM images and EELS measurements along the interface we can determine that each element attaches to the interface differently depending primarily on atomic size. Elements with the smallest atomic radius (Lu) appear to attach to the Si₃N₄ prismatic 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 atom (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 Imaging of Multiple 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, E_p , is related to the valence electron density, n , as $E_p \cong [(h/2\pi)w_p^f]^2 + E_g^2]^{1/2}$. Here $w_p^f = [ne^2/(\epsilon_0 m)]^{1/2}$ is the free electron plasma frequency, e is the electron charge, ϵ_0 is the permittivity of vacuum, m is the electron mass, and E_g is the bandgap energy. Furthermore, we have established universality and scaling in relations between E_p , electron density at the boundary of Wigner-Seitz (WS) cells and experimental and ldf calculated elastic constants and hardness for a number of single crystal and polycrystalline metals, nonmetals, metalloids and compounds that follow the universal binding energy relation (UBER). Its origin lies in the nature of electron-ion (atom nuclei) interactions and in the exponential decay of n with interparticle separation, or into interstitial sites, since the scaled cohesive energy, $E^* = E/\Delta E_{coh}$, atomic separation, $a^* = (a - a_m)/l$ (ΔE_{coh} is the equilibrium cohesive energy, a_m is the equilibrium interatomic spacing) can be described by a Rydberg type function, $E^*(a^*) = -(1 + a^*)e^{-a^*} = -(1 - \ln a^*)n^*$. The scaled density is defined here as, $n^* = [n/n_m]^\gamma = e^{-a^*}$, n_m is the density at the energy minimum and γ is the second derivative of $E(n)$ at equilibrium. Both E_p^2 and the bulk modulus, B_m , $\propto n$, since $B_m = (1/12\pi)r_{wse}^{-3}\Delta E_{coh}\eta^2$, where r_{wse} is the equilibrium WS atomic radius, l is the characteristic length describing the width of the binding energy curve and $\eta = r_{wse}/l$ is the anharmonicity parameter. As a consequence, we found a strong scaling of E_{coh}/V_{wse} , n and elastic constants with E_p of the power type $P_m = AE_p^B$, where A , B are lsf coefficients that depend on the structure and bonding. One can measure E_p and use scaling to image and/or predict the local properties with nanometer spatial resolution. This is illustrated for metastable, 25-70 nm thick, lath-shaped γ -TiH_x precipitates that form on the {01 $\bar{1}0$ } planes in the α -Ti matrix on ageing and cause severe embrittlement in Ti alloys. α -Ti has a plasmon peak at 17.7 ± 0.1 eV and the estimated $B_m = 85.2$ GPa, or 21.4% less than the reported value for Ti. For TiH_x, the plasmon is 2.4 eV higher, indicating that the TiH_x particles are stiffer than the surrounding matrix with the moduli 30-40 GPa higher, thus explaining the propensity for cracking through the hydrides and/or along the hydride/Ti interface. Dividing a 20 eV plasmon TEM image of the precipitates, by an 18 eV image acquired over the same area with a 3 eV window, essentially removes thickness and diffraction effects. Such a ratio-image, with the linearly varying intensity allows distinction between the precipitates and the matrix. The maps (line profiles) of elastic constants, E_{coh}/V_{wse} and n_b have been derived by rescaling the ratio-image within the selected range of energy losses followed by calculation of the parameters for each pixel using related scaling equations.

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 and Paul A. Midgley¹; ¹Department of Materials Science and Metallurgy, University of Cambridge, Cambridge, United Kingdom; ²Department 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 semi-conductor 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 to experimental data. 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.

P3.3

Electron Holographic Characterization of Nano-Hetero Interface Effect in Gold Catalysts. Satoshi Ichikawa, Tomoki Akita, Kazuyuki Okazaki, Koji Tanaka and Masanori Kohyama; Research Institute for Ubiquitous Energy Devices, National Institute of Advanced Industrial Science and Technology (AIST), Ikeda, Japan.

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 have relation to the change of the electronic state near the interface between the gold particles and the oxide supports. But it has not been clear yet. Using high resolution electron microscopy (HREM) and electron holography, we investigated the atomic structure near the interface and the size dependence of the mean inner potential of gold in Au/TiO₂ catalysts prepared by the deposition precipitation (DP) method and the vacuum evaporation (VE) method. The TiO₂ supports prepared by DP method and VE method are considered to have oxygen-rich surfaces and titanium-rich surfaces respectively. In case of the Au/TiO₂ catalyst prepared by DP method, 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 indicates that the electronic state of gold on TiO₂ changes 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 one of the dominant reasons for the behavior difference of the size dependence of the mean inner potential between the preparations.

P3.4

High Spatially Resolved EELS Imaging Technique for Plasmon Loss Energy Distribution Measurement in Amorphous Aluminum Oxide Thin Films. Mitsuho Koike, 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 images for the 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 ordinary greater than 1.0 eV. 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 silicon substrate were acquired with a parallel type detector (Gatan Model 666) attached to an 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 was 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 images from 255 SREELS spectra, and found slight fluctuation of plasmon loss peak energy, within the range from 22.5 eV to 23.0 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 insulative, W. Tews and R. Gründler¹ 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 suggests that we can evaluate the mass density ρ by measuring the plasmon energy using Bell's model². 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 ($\Delta\rho$) in our method was approximately 0.1 g/cm³. The spatial 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. **References** 1) W. Tews and R. Gründler, phys. stat. sol., (b) 109, 255 (1982) 2) F. G. Bell and L. Ley, Phys. Rev. B 37, 8383 (1988)

P3.5

The Electron Microscopy and XRD Investigation of Structure Processes in CMR Crystals LaMnO₃+d. Veniamin Shekhtman, Vera Sedykh, Natalia Afonikova, Aleksey Dubovitskii and Valery Kulakov; Institute of Solid State Physics RAS, Chernogolovka, Russian Federation.

The compounds of manganites possessing colossal magnetoresistance belong to a wide structure perovskite family and have various magnetic and transport properties. An important specific feature of this system is the influence of the variations of synthesis, annealing and quenching conditions of the compound on the appearance of the specific atomic-structural configuration. Three main structural modifications of the compound with the common formula LaMnO₃+d: trigonal R-3c, orthorhombic PnmaI and PnmaII. The specific feature of this system is the influence of the variations of synthesis, annealing and quenching conditions of the compound on the appearance of the specific atomic-structural configuration. Besides the phases of LaMnO₃+d can be reversibly transformed to each other under appropriate annealing. It is known also that mutual structural readjustments of these phases are definitely monitored by a relatively small parameter of extra oxygen. In the connection of aforesaid the analysis of the properties of the given system has been carried out using the complex of structure methods - electron microscopy, electron diffraction analysis, low-temperature XRD experiments "in situ". The X-ray diffraction analysis of the investigated compounds has been conducted in the temperature range down to T= 93K. The specific features of the mutual basic adjustments and atom-scale behavior under reversible structure transformations have been described. The data of the appearance of the intermediate phase with the modulated structure in the non-doped manganite at the specified conditions in addition to the known structural modifications are discussed. The results of the analysis of the modulated structure by the electron microscopy and electron diffraction methods are presented. The specific features of the atom-scale behavior at the mutual transitions between structural modifications are considered. It has been shown that the appearance of structural modifications is an intermediate step at the mutual transitions between two orthorhombic modifications. The work was supported by the Russian Foundation for Basic Research (project 03-02-17232).

P3.6

Similarities in the Local Order in Single Grain Cd-Yb Approximant and Quasicrystalline Phases. Y. Q. Wu, M. J. Kramer, Dongmei Wu and T. A. Lograsso; Metals and Ceramics Sciences, Ames Lab. ISU, Ames, Iowa.

Large single crystals of the B.C.C. approximant Cd₈₆Yb₁₄ phase were studied at the atomic scale using high resolution transmission electron microscopy (HRTEM). Based on previous studies on the local order in binary QC icosahedral phase of Cd₈₄Yb₁₆, the QC structure is believed to form by an aperiodic packing of a four-shell clusters arrangement observed in the approximant crystal phase. Therefore, it is very necessary to study the relationship between local and long-range order in the QC phase and its corresponding approximant phase. The B.C.C. approximant Cd₈₆Yb₁₄ phase was made by using the Bridgman method. Foils for HRTEM were electron discharge machined from larger grains on the order of 0.75 cm³ and mechanically thinned to 200 μm then electropolished. Through-focal images were obtained along [001] and [530] orientations, which correspond to the two-fold and five-fold directions of the nested Cd dodecahedron, Yb icosahedron and Cd icosidodecahedron clusters. The local atomic structures, i.e., the clusters, are shown to remarkably similar to the two and five-fold zones axes of the icosahedral Cd₈₄Yb₁₆ structure. Image reconstruction of the through-focal HRTEM images is being performed to obtain a 3D structure model, aimed at understanding the formation of the edge-sharing and overlapping of the four-shell clusters in the previously suggested for the QC icosahedral Cd₈₄Yb₁₆ phase (Y. Q. Wu, M. J. Kramer and T. A. Lograsso, MRS 2003 Fall Meeting).

P3.7

Effect of Simulated Body Fluid on the Microstructure of Ferrimagnetic Bioglass Ceramics. Nearchos Papanearchou¹, Angelica Hotiu¹, Theodora Leventouri¹ and Ian Anderson²; ¹Physics, Florida Atlantic University, Boca Raton, Florida; ²Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge,

Tennessee.

Series of Ferrimagnetic Bioglass Ceramics (FBC) were prepared in the system of oxides $[0.45(\text{CaO}, \text{P}_2\text{O}_5)(0.52-x) \text{SiO}_2x\text{Fe}_2\text{O}_3 0.03\text{Na}_2\text{O}]$, 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 magnetic measurements. A strong correlation between processing parameters, structure, microstructure and magnetism was discovered. Bioactivity of the FBC originates from the calcium phosphate $\text{Ca}_3(\text{PO}_4)_2$ that converts to bone-like hydroxyapatite, (HAP) $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, in a physiological environment. The magnetic properties of FBC arise from magnetite (Fe_3O_4) that is produced from the Fe_2O_3 of the starting oxides. The materials have been shown to be effective in hyperthermic treatment of animal bone cancer several years ago. Bioactivity of the systems was tested in vitro by emerging the samples in simulated body fluids (SBF) for various time intervals. XRD measurements reveal dependence of formation of the bioactive phase from the time period that the samples were exposed in SBF. Here we report on studies of the microstructure of the specimens before and after immersion in SBF. Dendrites of iron oxide with crystallites of various sizes form within a glassy matrix enriched in calcium, phosphorus, and silicon. The dendrite microstructure is affected by the composition of each system and the time period of exposure in SBF. 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.

P3.8

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 Axiovert 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. We are currently building a more sophisticated sample holder, presenting reduced condensation effects at the glass coverslip and improved temperature control to prevent contamination of the frozen sample (by crystalline ice and dirt particles). This second generation sample holder will ensure a higher resolution and reproducible working conditions. A key objective is the possibility of transferring the coordinates of the areas of interest, found on the frozen grid, directly from the light microscope to the electron microscope. MatLab-based software is being currently used to automate the sample observation, data collection and analysis for our FEI electron microscopes. 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.

P3.9

The Features of Investigations and Observations of Nanoamorphous Metals on Electron Microscope. Razmik Malkhasyan, Robert Karakhanyan, Armen Khachatryan and Mery Nazaryan; SPE ATOM, Yerevan, Armenia.

With the purpose of identification of amorphous materials transmission electron microscopes are widely used in the cases when the samples are nanosize and transparent for electron beam. The observation of diffractonal halo points to the presence of amorphous phase. However when working with nanosize amorphous metals in many cases the energy of beam is sufficient for essential transformations in examined sample. In the present paper it is shown that an electron beam influences actively on a sample subjected to an examination in two ways. In first case the active influence of a beam with its own charge leads to destruction of agglomerates from nanoparticles, as if forming a fine sand from separate nanoparticles that enables to determine a real magnitude of a grain of the given nanomaterial. This positive factor also enables to observe that real picture which we have in a sample, but which at first is latent by

coating from nanoparticles and their agglomerates. For example, removal of nanopowder coatings has enabled for the first time to find self assembling systems in a shape of double spatial helixes from inorganic particles (like DNA). The second type of influence is bound up with transformations which distort the sample. Transformation of amorphous particles of metal into a crystalline state by means of local heating of these particles is the most important type of influence for us. The phenomenon of dissociation of crystalline salt to amorphous components and the further crystallization of these new particles was observed. Growth of thread shaped hollow and solid nanowhiskers from nanoparticles and their further disintegration to a great number of small crystals under influence of electron beam in the chamber of electron microscope. Therefore one can confirm that it is necessary to use an electron microscope with special precautionary measures, when working with nanoamorphous metals.

P3.10

Transmission electron microscopy study on the domain structures in ferroelectric $\text{SrBi}_2\text{Nb}_2\text{O}_9$ ceramics. Karthik Chinnathambi, 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 $\text{SrBi}_2\text{Nb}_2\text{O}_9$ (SBN) ferroelectric ceramics which belong to the Aurivillius family of Bi-layered perovskite oxides. SBN is a potential candidate for NVRAM applications. The 90° 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 90° domain walls are irregular in shape. The Antiphase boundaries are less dense as compared to that of $\text{SrBi}_2\text{Ta}_2\text{O}_9$. 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

P3.11

Effect of Inversion Boundaries on the Grain Growth of ZnO. Sae-Jin Kim, Wook Jo and Doh-Yeon Kim; School of Materials Science & Engineering, Seoul National University, Seoul, South Korea.

To make ZnO-varistors, Bi_2O_3 and other oxides are usually added. When TiO_2 is added, it is known that the incoherent inversion boundaries are formed and the grain growth is promoted. On the other hand, when Sb_2O_3 is added, the coherent inversion boundaries are formed and the grain growth is inhibited. In this study, etching patterns and the crystallographic characteristics of the inversion boundaries in ZnO were analyzed. Twin planes of incoherent inversion boundaries with TiO_2 addition and coherent inversion boundaries with Sb_2O_3 addition were determined to be $\{000\text{-}1\}$ and $\{0001\}$ plane, respectively. In this talk, we will discuss the relationship between the structure of inversion boundaries and the grain growth behavior.

P3.12

The Nucleation and Growth of Nanoscale Ni Particles on Single Crystal TiO_2 Substrates by In-Situ UHV TEM. Xiaoqing Pan, Yanbin Chen and Haiping Sun; Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan.

Nanosized Ni particles grown on single crystal TiO_2 surface form a model system for both surface science and catalysis research. In this work we studied the nucleation and growth of nanosized nickel (Ni) particles on the (100) and (110) surfaces of the rutile TiO_2 substrates using an in-situ ultrahigh-vacuum transmission electron microscope (TEM) equipped with two electron beam evaporators. The formation of nanosized particles and the evolution of their morphology and structure were observed in real time during deposition. The analysis of diffraction patterns shows that the Ni particles grow epitaxially on both (100) and (110) surfaces of TiO_2 with the orientation relationships of Ni (110) $[-220]//\text{TiO}_2$ (100) $[002]$ and Ni (110) $[00\text{-}2]//\text{TiO}_2$ (110) $[-110]$, respectively. These orientation relationships are favorable in the minimization of the total energy according to first principle calculations using the density functional theory.

P3.13

HREM Imaging of Screw Dislocation Core Structures in bcc Metals. B. G. Mendis and Kevin J. Hemker; Mechanical Engineering, Johns Hopkins University, Baltimore, Maryland.

Screw dislocations in body centered cubic (bcc) metals have been the subject of extensive theoretical studies since it was first realized that the core may dissociate along three $\{110\}$ type planes that contain the dislocation line vector. The intrinsically high Peierls-Nabarro stress, resulting from the non-planarity of the core, means that pure screw dislocations are considerably less mobile than edge dislocations, and therefore play an important role in the macroscopic deformation

of bcc metals and alloys. Simulations have also shown that non-glide stresses alter the core structure by changing the edge displacements of the core atoms. 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 effects of specimen thickness and electron optic parameters on the appearance of the edge displacements for screw dislocations in bcc molybdenum. The dislocation configurations used in the simulations are based on atomistic and first principle calculations. In addition surface relaxation of the foil (i.e. the Eshelby 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 Ziegler¹, James M. McNaney², Michael J.

Hoffmann³ and Robert O. Ritchie^{1,4}; 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, Berkeley, California.

The effects of grain-boundary chemistry on the mechanical properties of high-purity silicon nitride ceramics have been investigated, 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 a high-purity Si3N4 processed 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 correlated to 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 debonding 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 debonding 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=0.3923nm, 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 in Si-based devices due to interfacial stability between 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 novel metals and SrTiO₃ (100) substrate, study on the interface between Pt and SrTiO₃ (111) is an undeveloped area and has an importance of unique basic data for the electronic device development. The study on the interfacial structure between Pt and SrTiO₃ (111) was consisted of three parts. First, Pt thin film should be epitaxially grown on the SrTiO₃ (111) substrate. In order to obtain perfect interface for transmission electron microscopy (TEM) analysis, the surface termination of SrTiO₃ (111) substrate should be needed. SrTiO₃ (111) is unstable due to a polar surface with Ti(4+) and SrO₃(4-) and the surface reconstruction can be easily generated on SrTiO₃ (111). Therefore, the condition of surface termination is very sensitive so that previous researches for surface termination have a low reliability for formation of step terrace. Our new method for surface termination of SrTiO₃ (111) is very easy and reliable so that the step terraces with same chemical state and width can be successfully obtained. In our method, SrTiO₃ (111) substrates were etched in NH₄F solution during 2min and annealed in tube furnace

with oxygen atmosphere at 850°C during 60 min. Through NH₄F etching, many hillocks with same edge direction were densely generated on SrTiO₃ (111) surface and changed to step terrace after oxygen annealing. Structural and chemical characteristics of hillocks and terminated surface have been analyzed by TEM and middle energy ion spectroscopy (MEIS). Also, mechanism and process of surface termination will be precisely discussed by in-situ heating TEM analysis. Second, in progress, interfacial atomic arrangement between Pt and SrTiO₃ (111) has been analyzed by using high resolution electron microscopy (HREM) and HREM simulation. Third, chemical structure between Pt and SrTiO₃ (111) has been investigated and discussed by using energy loss near edge structure (ELNES) and ELNES simulation.

P3.16

Abstract Withdrawn

SESSION P4: Three Dimensional Nanoscale Characterization

Chairs: Christian Kuebel and David Martin
Tuesday Morning, November 30, 2004
Gardner (Sheraton)

9:00 AM *P4.1

High-Resolution 3D Structural Characterization in Physical Sciences - TEM and HAADF-STEM Tomography.

Christian Kuebel, Application Laboratory, FEI Company, Eindhoven, Netherlands.

With the recent advances in nanotechnology and the semiconductor industry, there is an increasing demand for high-resolution 3D structural information in the physical sciences, especially as the dimensions and geometrical complexity in these areas are starting to approach those observed in the life sciences. As the size of the features of interest is approaching the thickness of the TEM sample, the interpretation of a single 2D projection is becoming increasingly difficult. For example, in the semiconductor industry, one common problem in metrology and defect analysis is that the projection of small (curved) device features averages out the structure of interest in a single 2D image, thereby preventing direct, reliable analysis. In addition, for catalysis applications, the analysis of the porosity of the support material together with the (size) distribution of the active catalyst requires 3D information with a resolution in the low nanometer range. Electron tomography is currently the only technique that can provide nanometer resolution in three dimensions for a "large" volume. However, TEM tomography, which is well established in life sciences, is only of limited use in physical sciences as diffraction contrast in TEM images results in artifacts and blurs the 3D reconstruction. Therefore, we have developed HAADF-STEM tomography, which can be used for a wide range of amorphous to highly crystalline materials, all the way from self-organized block-copolymers to catalysts, hydrogen storage materials and various semiconductor materials to mention just a few examples we have worked on in the last 3 years. Typically, a resolution of about 3-5 nm can be achieved in 3D for beam stable materials with sample thicknesses of 150-300 nm, but in some cases even particle sizes with a FWHM of about 1.5 nm could be reliably measured and, in the case of heavy particles, sub-nanometer particles could be detected in 3D. In order to exemplify the possibilities of electron tomography in physical sciences, several application examples will be presented, mainly focusing on catalysts and semiconductor materials. I will show how the morphology, particle size distribution and surface variations can be analyzed in 3D. Finally, the advantageous and limitations of both TEM and HAADF-STEM tomography for materials science will be discussed.

9:30 AM *P4.2

Observing the Dynamics of Molecular Machines by 3D Cryo-EM - Potential and Limitations as Exemplified by the Ribosome. Joachim Frank, Wadsworth Center, Albany, New York.

The method of single-particle reconstruction [1, 2] is based on the premise that a large number of molecules, ranging in the tens of thousands, have identical structure but present different random orientations on the specimen grid. By using single-particle reconstruction in combination with cryo-EM, molecular machines can be imaged at different stages of their work in close to native conditions, provided it is possible to trap all molecules in distinct functional states. A wealth of data has been obtained for the ribosome and its cyclic interactions with mRNA, tRNA, and the elongation factors during the course of protein synthesis [3]. Trapping in defined states may be achieved by using antibiotics, or nonhydrolyzable analogs of GTP, the molecule providing energy for some of the reactions. One could call the reconstructions of the ribosome achieved in this way "3D snapshots". Such snapshots make it possible to follow

the dynamics of the molecular processes crudely. The question is how to fill the gaps in between. In some cases, intermediate states may exist whose lifetime is long enough to be recorded – in this case, classification techniques must be employed to sort out heterogeneous ensembles of particles. In general, there is a need to complement the information obtained by 3D cryo-EM snapshots with data obtained by other methods such as FRET or MD simulations. [1] J. Frank (1996), Three-dimensional Electron Microscopy of Macromolecular Assemblies. Academic Press, San Diego. [2] J. Frank, P. Penczek, R.K. Agrawal, R.A. Grassucci, and A. B. Heagle (2000) Three-dimensional cryoelectron microscopy of ribosomes. *Meth. Enzym.* 317, 276-291. [3] J. Frank (2003) Electron microscopy of functional ribosome complexes. *Biopolymers* 68, 223-233.

10:30 AM P4.3

Image-Based Nanocrystallography by Means of Transmission Electron Goniometry. Peter Moeck¹, Bjoern Seipel¹, Wentao Qin² and Phil Fraundorf³; ¹Department of Physics, Portland State University, Portland, Oregon; ²Technology Solutions, Freescale Semiconductor, Chandler, Arizona; ³Department of Physics and Astronomy and Center for Molecular Electronics, University of Missouri, St. Louis, Missouri.

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 nanocrystallography 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 high resolution 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.

10:45 AM P4.4

Solving Complex Three Dimensional, Nanoscale, Structural Problems by Application of Emerging New Modes of Electron Tomography. Matthew Weyland¹, Paul Midgley² and David A.

Muller¹; ¹Applied and Engineering Physics, Cornell University, Ithaca, New York; ²Materials Science and Metallurgy, University of Cambridge, Cambridge, United Kingdom.

The technique of electron tomography has, in recent years, broadened its application into materials science through the application of novel imaging techniques; such as high angle annular dark field (HAADF) 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. In addition results will be presented of 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 as well suited, if 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.

11:00 AM P4.5

Discrete Tomography of Ga and InGa Particles from HREM Image Simulation and Exit Wave Reconstruction. Joerg R.

Jinschek¹, Joost Batenburg², Hector Alfredo Calderon³, Dirk Van Dyck⁴, Fang R. Chen⁵, Velimir Radmilovic¹ and Christian Kisielowski¹; ¹National Center for Electron Microscopy, Ernest Orlando Lawrence Berkeley National Laboratory, Berkeley CA, California; ²Mathematical Institute, Leiden University, Amsterdam, Netherlands; ³Ciencia de Materiales, ESFM-IPN, Mexico, DF, Mexico; ⁴EMAT, University of Antwerp (RUCA), Antwerp, Belgium; ⁵Center of Electron Microscopy, National Tsing Hua University, HsinChu, Taiwan.

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 atomic column. This concept has been tested in the present investigation where HREM image simulation (MacTempas[®]) together with exit wave reconstruction (FEI TrueImage[®]) have been performed. A cubeoctahedral 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], [011]) have been used and the parameters of an aberration corrected microscope (200 kV, Cs = 0 mm, 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 position of all 309 atoms and the 3D shape of the nanocrystal. Additional results and limitations of the method as well as requirements for performing the real experiment will be discussed.

11:15 AM P4.6

Three-Dimensional Characterization of the Structural Properties of Quantum Dots. Ilke Arslan¹, Timothy J. V. Yates¹, Matthew Weyland², Paul A. Midgley¹ and Nigel D. Browning³; 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.

While nanotechnology presents many exciting opportunities for materials science, it also presents significant challenges for characterization. These challenges arise because optimizing the functionality of nanoscale materials often depends on a precise control of the size, shape, crystal structure and composition of the material(s) being synthesized. While traditional techniques in transmission electron microscopy have provided feedback for the growth of single crystal films and polycrystalline solids (where crystal/defect structure/composition are the property determining factors), the application of these techniques to nanoscale particulates (where size and shape are important) is not as straightforward. However, the ability to characterize all the above listed features is now possible through the combination of Z-contrast imaging (including 3-D tomography) and electron energy loss spectroscopy (EELS) in the scanning transmission electron microscope (STEM). An example of what can be achieved with these techniques is illustrated by the analysis of Sn quantum dots (QDs) embedded in a Si matrix. A 2-D analysis of this material shows that the dots' shapes resemble rhombohedrons that are bounded by the {111} facets and where the corners are rounded by {110} and {100} facets. An EELS analysis reveals a particularly intriguing feature of these quantum dot structures; that the amount of Sn varies from dot to dot, despite having the same size. This composition variation has been determined to arise from the dots being formed through the filling of voids in the Si substrate. However, what cannot be determined from the image is whether the filling of the voids takes place through a coating of the inside surface or a filling up of the voids from one side. Only through 3-D imaging can the shape of these QDs be fully characterized. Analysis of these samples in three dimensions using electron tomography clearly show the size and position of the quantum dots in the buried layer. It can be seen that although there is a size variation, there is a regular shape and clear faceting observed for all of the quantum dots. A full analysis of these structures will be presented.

11:30 AM P4.7

STEM-based mass spectroscopic study of supported metal nanoparticles. Huiping Xu¹, Laurent Menard², Anatoly Frenkel³, Ralph Nuzzo², Duane Johnson⁴ 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.

The success of future applications of metal nano-clusters in heterogeneous catalysis depends on the full understanding of their supported three-dimensional structure [1]. As the nanoclusters become smaller, completely different catalytic activity has been observed in some systems, such as Pt-Ru and gold nanoparticles. Yet, the 3-dimensional exact structure and bond information of these supported nanoparticles 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 1nm or 100 atoms per cluster. Quantitative Z-contrast imaging or very high angle (96mrad) annular dark-field (HAADF) imaging in a dedicated scanning transmission electron microscopy is a novel and emerging technology in determining the exact number of atoms in a cluster through quantification of absolute image intensity and our newly developed robust interactive computer program[2], instead of traditional particle size measurement. We have previously determined the number of atoms in very small clusters, such as Re_6 and PtRu_5 nanoclusters [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) techniques 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 our newly synthesized thiol-stabilized gold particles, which have been shown by TEM to be of sub-nanometer size (0.84nm) and highly monodisperse narrow distribution. Current efforts are focused on analyzing quantitatively and comparing 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 nanoclusters. [1]. G. Schmid et al., Chem. Soc. Rev., 28, 179 (1999). [2]. J.C. Yang, S. Bradley and J.M. Gibson, Microsc. Microanal., 6, 353 (2000). [3] J.C. Yang, S. Bradley, J.M. Gibson, Materials Characterization, 51, 101 (2003). [4]. A. Singhal, J.C. Yang and J.M. Gibson, Ultramicroscopy, 67, 191 (1997). Supported by the Department of Energy (#DE-FG02-03ER15475).

11:45 AM P4.8

3-D Atom Probing for Elemental Identification in Si Nanostructures. Keith Thompson, Tom Kelly, Tye Gribb and Rob Ulfig, Imago Scientific Instruments Corporation, Madison, Wisconsin.

The aggressive down-sizing of conventional Si devices and the introduction of novel nano-devices has driven and will continue to drive the technological advance of electronics for the next two decades. These ultra-small devices require extraordinarily novel diagnostics techniques in order to monitor the effects of macro-processing on the nano-scale, to correlate the discovery of new nanoscale phenomena to macro-recorded events, and to enable the investigation of local anisotropies in devices to electrical performance. Ideally, one would like to map the location and identity of every atom within a nanostructure. The evolution of 3-D atom probing, most specifically through the utilization of a local electrode, has enabled exactly this sort of metrology. This diagnostic has opened up the possibility of obtaining experimental data in research areas that previously have only been analyzed via theoretical characterization and advanced computer modeling. So far, this technique has successfully been applied to the study of nanostructures in magnetic materials, super alloys, and designer metals. Recently we have applied this technique to semiconductor nano-devices. We have demonstrated that our Local Electrode Atom Probe (3D-LEAP) can successfully map the location and identity of dopant atoms in Si, can identify clusters of atoms and grain boundaries in poly or crystalline Si, and can effectively monitor the diffusion of metal atoms within other metal films and within Si. We will give a short background of 3-D LEAP technology and then demonstrate its application to the semiconductor field by presenting atomic maps that show: (1) bulk doping of B, P, Sb, and As in Si; (2) graded dopant distributions of Sb and Ga in Si; (3) 3-D distribution of B dopants in poly-Si with B clusters and poly-Si grain boundaries; and (4) the inter-diffusion of Co and Ni within the Co, Ni, and Si layers.

SESSION P5: Quantitative Electron Microscopy:
Holography, Dopant Profiling and Diffraction
Chairs: Paul Midgley and Paul Voyles
Tuesday Afternoon, November 30, 2004
Gardner (Sheraton)

1:30 PM *P5.1

Novel approaches for the characterization of electromagnetic fields using electron holography. Rafal Dunin-Borkowski¹ and Takeshi Kasama^{2,1}, ¹University of Cambridge, Cambridge, United Kingdom; ²RIKEN, Wako, Saitama, Japan.

Electron holography is a powerful technique for mapping magnetic and electrostatic fields in the transmission electron microscope. I will illustrate new approaches that are being developed to characterize nanoscale materials and devices that have feature sizes of between 5 and 100 nm. Examples will be taken from the characterization of electrical and magnetic circuits that have voltages applied to them in situ in the electron microscope, and from the development of analytical techniques that allow vector and scalar fields to be measured in three dimensions from recorded phase images.

2:00 PM P5.2

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 far as a detectable electrostatic potential distribution is formed by active dopant atoms in a semiconductor even if their densities are too thin to be detected. Future applications are promising, as the dimension of the device will be decreased, the high spatial resolution of the method compared with other possible dopant profiling techniques would be advantageous. In order for the method to become a reliable characterization tool, however, 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 or 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 converter and we proved that a nearly 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 simulator have proved that they are in good agreement. [1] A. Tonomura, 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] Gribelyuk M. A., McCartney M. R., Li J., Murthy C. S., Ronsheim P., Doris B., McMurray J. S., Hedge S., and Smith D. J., Phys. Rev. Lett. 89 (2002) 25502. [4] T. Matsumoto, et al., to be published.

2:15 PM P5.3

Three-dimensional analysis of the dopant potential of a silicon p-n junction. Alison Twitchett¹, Rafal Dunin-Borkowski¹, Simon Newcomb² and Paul Midgley¹, ¹Materials Science, University of Cambridge, Cambridge, United Kingdom; ²Sonsam 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 fully quantitative results, the measured potential is 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. A 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 70° 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. Twitchett 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 (Vic) Liu¹, Dean J. Miller¹, J. Tao², J. M. Zuo²

and S. Marchesini³, ¹Materials 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 RAAR (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,

3:45 PM P5.6

Accurate Determination of Orientation Relationships between Ferroelastic Domains: The Tetragonal to Monoclinic Transition in LaNbO₄ as an Example. Øystein Prytz and Johan Taftø; 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 I2/a (C2/c) with a monoclinic angle $\beta=94.1^\circ$. This system serves as a useful model of a ferroelastic transition of the $4/m\bar{F}2/m$ type using the notation of Aizu [1]. This transition produces ferroelastic domains, the boundaries between which are parallel to the monoclinic b-axis. The orientation of these boundaries relative to the monoclinic a- and c-axes has been predicted by Sapriel [2] for all 94 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)/(4.04 0 2) 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] K. Aizu, *Phys. Rev. B* 2, 754-772 (1970). [2] J. Sapriel, *Phys. Rev. B* 12, 5128-5140 (1975). [3] L. Jian and C. M. Wayman, *J. Am. Ceram. Soc.* 79, 1642-1648 (1996). [4] S. Tsunekawa and H. Takei, *Phys. Stat. Sol. (a)* 50, 695-702 (1978). Acknowledgements The authors would like to acknowledge Drs. Yu. M. Baikov and B. T. Melekh of the Ioffe Physico-Technical Institute, St. Petersburg, Russia, and Professor Truls Norby of the Department of Chemistry, the University of Oslo for providing the materials used in this study.

4:00 PM P5.7

Microstructure of Phase-Transformed Tantalum Thin Films. Katherine Jackson¹, Robert Knepper¹, Eric A. Stach² and Shefford P. Baker¹, ¹Department of Materials Science & Engineering, Cornell University, Ithaca, New York; ²National Center for Electron Microscopy, Lawrence Berkeley National Laboratory, Berkeley, California.

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) and transmission electron microscopy (TEM). Analysis indicates the

4:30 PM **P5.9**

The Characterization of Imaging and Analysis Performance of Modern TEM and STEM Systems. Sergei Lopatin¹, Nigel D.

Browning^{1,2}, Bernd C. Kabius³ and Nestor J. Zaluzec³; ¹NCEM, Lawrence Berkeley National Laboratory, Berkeley, California; ²Chemical Engineering and Materials Science, University of California-Davis, Davis, California; ³Materials Science Division, Argonne National Laboratory, Argonne, Illinois.

;&P ALIGN=JUSTIFY> The field of electron microscopy is undergoing a revolution based on major recent advances in electron optics, detectors, stage design and computing power. These advances make it possible to overcome the fundamental limitations currently imposed by lens aberrations. The resulting leap in performance will lead to a new generation of electron microscopes, which will feature substantial advances in spatial, temporal and spectral resolution, providing unprecedented scientific opportunities for atomic level characterization of materials. To design a new type of electron microscopes around aberration corrected optics it is necessary to evaluate the potential for the main column components (gun, monochromator, aberration-corrector, detectors, etc) to be integrated into a single column. Such evaluation requires to develop systematic procedures for testing and comparing of existing TEM and/or STEM columns in terms of spatial, temporal and spectral resolution in a variety of practical applications. Moreover, not just the "individual" resolution but the limits of simultaneous energy and spatial resolution as well as heavy and light elements sensitivity (s/n ration) need to be established. For that purpose a number of test samples such as GaAs/AlAs super-lattice with varying layer thicknesses, CdSe/Te nano-particles, Gold film, and SrTiO₃ can be utilized. Such a set of samples will be used for the standard instrument resolution tests and measurements on the modern TEM and STEM systems from major manufacturers with different configurations of monochromators/correctors. The results of those tests will be presented and the subsequent analysis of column components compatibilities and the limitations they might impose on materials structure characterization will be discussed.

4:45 PM **P5.10**

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

B. G. Mendis, I. P. Jones and R. E. Smallman; Metallurgy and Materials, University of Birmingham, Edgbaston, United Kingdom.

In a face centered cubic alloy dissociation of a perfect 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 atom segregation or desegregation to the stacking fault plane, the sense of the solute redistribution being governed by the need to lower the energy 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 Suzuki segregation, 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 equilibria data. The discrepancy could either be due to experimental error or inadequacies in the theoretical model itself (e.g. by assuming that the planar fault has thermodynamic properties similar to a bulk hcp phase).

SESSION P6: Imaging Individual Structures and Defects in Bio- and Nano-Materials
Chairs: David Martin and Darrin Pochan
Wednesday Morning, December 1, 2004
Gardner (Sheraton)

8:30 AM ***P6.1**

Cryotransmission Electron Microscopy: An Integral Tool for Biological, Polymeric, and Self-Assembled Materials Characterization. Darrin Pochan,

¹Materials Science and Engineering, University of Delaware, Newark, Delaware; ²Delaware Biotechnology Institute, University of Delaware, Newark, Delaware.

Cryogenic imaging in transmission electron microscopy is rapidly becoming a routine technique for the characterization of in situ

solution structure. Having been pioneered in the fields of biology and surfactant science, cryoTEM is now being successfully applied to a much wider array of materials such as polymer solutions and inorganic-organic hybrid materials. Importantly, the direct observation of in situ structure provides a real-space compliment to small- and wide-angle scattering experiments. Recent cryoTEM results from a diverse collection of fields ranging from polymer self-assembly, surfactant and lipid science, and biology will be surveyed along with the basic sample and infrastructure requirements needed for successful cryoTEM materials characterization.

9:00 AM ***P6.2**

EELS of Biological Systems and Detection Limits.

Richard Leapman, Division of Bioengineering and Physical Science, National Institutes of Health, Bethesda, Maryland.

Recent developments in electron energy-loss spectroscopy (EELS) have created new opportunities for mapping the distributions of elements in biological systems. Optimized charge coupled device cameras have improved detection limits, while software programs for collecting and processing EELS data at each pixel in a spectrum-image have facilitated elemental analysis of isolated macromolecular assemblies as well as small organelles in sectioned cells. Useful information about the distribution of elements can be obtained even though radiation damage degrades the overall structure on a scale of several nanometers for EELS data collected either in the scanning transmission electron microscope (STEM) or in the energy filtering transmission electron microscope (EFTEM). STEM-EELS has been applied to map calcium in cellular compartments, to image phosphorus in nucleic acid-protein complexes, and to detect metal atoms contained in metalloprotein molecules. Calcium is a particularly important element because it regulates many biological processes. Analyses of spectrum-images acquired from freeze-dried cryosections of rapidly-frozen cells reveal how the calcium distributions are affected by conditions of stimulation. On a finer scale, by using a field-emission source that provides an electron probe of diameter 1 nm, it is possible to image single atoms of calcium in suitably thin specimens, and to detect the four iron atoms contained in a single molecule of hemoglobin. In biological systems, phosphorus and sulfur are typically present at atomic concentrations of 0.01 or lower, and calcium concentrations can be as low as 10 atomic parts per million. This often results in small signal-to-background ratios at the characteristic EELS core-edges, which makes the spectrum-imaging approach essential because it allows accurate subtraction of the background intensity at each pixel. The EFTEM provides a complementary quantitative approach for imaging cellular components that contain relatively high concentrations of specific elements, such as organelles rich in sulfur-containing proteins having large fractions of cysteine and methionine residues, or phosphorus-containing DNA in the cell nucleus. The advantage of EFTEM is that 10⁶ pixels can be acquired simultaneously from extended regions of a specimen, whereas in STEM the number of pixels that can be acquired in a reasonable period is limited by the minimum readout time of the EELS detector. By combining electron tomography with EFTEM, it has recently been possible to determine the three-dimensional distributions of phosphorus in unstained eukaryotic cells prepared by high-pressure freezing, freeze-substitution, plastic embedding and sectioning. Those experiments have revealed the distributions of nucleic acid-containing ribosomes throughout the volume of an unstained cell with a sensitivity of about 30 phosphorus atoms per voxel.

9:30 AM **P6.3**

Mapping the Structure of Solvated Polymers Using

Energy-Loss Spectroscopy in the Cryo-STEM. Alioscka Sousa, Sergey Yakovlev and Matthew R. Libera; Chemical, Biomedical and Materials Engineering Department, Stevens Institute of Technology, Hoboken, New Jersey.

Dissolved solvents are known to play a key role in determining many important polymer properties. Biological response to a polymer surface, for example, is often determined by the local level of hydration at length scales associated with cells and adhesion-mediating proteins. Likewise, molecular permeability is often determined by the length scale and degree of percolation associated with solvent-rich paths in polymer membranes. Despite its importance, however, there has not yet been much experimental work performed to correlate solvent distribution at micro and nano length scales with variations in underlying polymer morphology due to, for example, phase separation or crystallinity. Because of its combined spectral sensitivity and spatial resolution, we are exploring the use of electron energy-loss spectroscopy (EELS) in the cryo-STEM to study solvated polymers. The spatial resolution is limited by the radiation sensitivity of the solvated polymers rather than by the optics of the microscope. Solvated polymers are more radiation sensitive than dry polymers, and we quantify damage by multiple least squares fitting using damaged and undamaged reference spectra. We discuss resolution using the Rose criterion, which quantifies the tradeoff

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 thin films of the organic semiconductor pentacene, multi-block copolymers, electrospun nanofibers, biological microtubules and biopolymer thin films. A detailed description of electron-sample interactions at 5 kV is presented, along with a 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 approximated 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. Multi-slice calculations of microtubules 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 Wang^{1,2}, Yaofeng Chen¹, Yunyi Fu¹, 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 typical diameters of 20-60 nm and lengths from several to tens of micrometers. Besides the single crystal Fe₂O₃ nanowires, a great amount of bicrystalline nanowires can also be found with ellipsoidal heads. Investigations indicate that most of the bicrystalline nanowires are nano-twins and their orientation relationship is obtained to be $(-1,1,10)M//(-1,1,10)T$, $[110]M//[1-10]T$. High resolution TEM with numerical reconstruction procedures have also been used to investigate the atomic structure of the micro-twins and the atomic 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 973 projects (MOST, No 2002CB613505) 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.

Alejandra Camacho-Bragado¹, Jorge A. Ascencio² and Miguel Jose Yacamán^{3,1}; ¹Texas Materials Institute, University of Texas Austin, Austin, Texas; ²Programa de Investigacion y Desarrollo de Ductos, Instituto Nacional del Petroleo, Mexico City, Mexico; ³Chemical Engineering, University of Texas Austin, Austin, Texas.

There were synthesized very large films of self-assembled molybdenum sulfide nanoribbons. Molybdenum sulfide nanotubes 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 a hydrothermal reaction 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 resulting 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

Shapley², Anatoly Frenkel³, Duane Johnson⁴, Charles J. Werth⁵ 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 to nitrogen alone, as the net release of ammonia is also significantly higher than permitted levels. We hypothesize that different Pd/M (M=Cu, Sn, In, Pt, Ag, Co, Fe, Mo, Ni, Rh, Ir, Mn and Cr) combinations on unique support structures can yield significant improvements to both nitrate reaction 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 (96mrad) annular dark-field imaging is that the intensity of the (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. Viraraghavan, 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. Jingshan 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 soap and silver nitrate. Cryo-TEM, together with an on-the-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 d-spacing of the final crystals. Those particles aggregate to produce larger and loosely packed embryonic crystals, the precursors to the ultimate silver stearate crystals.

11:30 AM P6.9**Direct Imaging of Quantum Anti-Dots in Au Nano-Cluster Dispersed TiO₂, SrTiO₃, and MgO.** Chongmin Wang¹, V.

Shutthanandan¹, Y. Zhang¹, S. Thevuthasan¹ and G. Duscher^{2,3}; ¹Environmental Molecular Science Laboratory, Pacific Northwest National Laboratory, Richland, Washington; ²Materials Science and Engineering, North Carolina State University, Raleigh, North Carolina; ³Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Dispersion of gold nanoclusters in single crystal TiO₂, MgO, and SrTiO₃ have 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**HREM Chemical and Structural Analysis of the Central Dark Line Defect of the Human Tooth Enamel.** Jose Reyes-Gasga and Ana Guadalupe Rodriguez-Hernandez; Instituto de Física, Universidad Nacional Autónoma de México, México, D.F., México, D.F., México.

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 Electron 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 gave 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, J. Canetas, M. Aguilar, S. Tehuacanero, C. Flores, C. Magana, C. Zorrilla, and A. Sanchez. This work was experimentally supported by DGAPA-UNAM with the project IN-104902.

SESSION P7: In-situ Microscopy of Deformation and Growth (Even in Liquids)

Chairs: 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 Cumings¹, David Goldhaber-Gordon¹, A. Zettl^{2,3}, M. R. McCartney⁴ and J. C. H. Spence⁵; ¹Department of Physics, Stanford University, Stanford, California; ²Department of Physics, University of California, Berkeley, California; 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 electrical and mechanical 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 and pitfalls 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 concentrically packed tubular sheets of graphite, where the 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 inside 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). This 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. Radisic², P. C. Searson², M. C. Reuter¹, 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 evaporation or 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 on the physical phenomena which 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 an external potentiostat. We will show simultaneous electrochemical and video-rate microstructural measurements of the nucleation and growth of copper clusters from acidified copper sulphate solution. Measurements of cluster growth kinetics clearly resolve the two expected limiting growth regimes, where cluster growth is controlled either by diffusion 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 nucleus density or the 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.

2:45 PM *P7.4

In Situ Microscopy of Nano-sized Metal Clusters: Challenges and Opportunities. Jeff T. De Hosson, Thomas Vystavel, George Palasantzas and Siete Koch; Applied Physics, University of Groningen, Groningen, Netherlands.

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 the clusters during deposition can be varied. 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 surface 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 excitations of the nanocluster deposition by starting with 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 Si₃N₄ 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). Annealing of clusters, which are in contact, leads to their fusion and formation of larger clusters preserving their crystallographic structure and being free of any oxide shell. During coalescence of the clusters of similar size the clusters rearrange themselves in an arc shape area where a finite size neck is formed leading thereafter to full coalescence. This observation is in contrast with theoretical descriptions of coalescence assuming initially a point contact as a pathway to coalescence.

3:30 PM P7.5

Effect of Sn on Roughening Transition Temperature of the Interface between Liquid Pb and Solid Al. Lihua Zhang¹, Erik Johnson² and Uli Dahman¹; ¹National Center for Electron Microscopy, Lawrence Berkeley National Laboratory, Berkeley, California; ²Nano Science Center, Niels Bohr Institute, University of Copenhagen, and 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 transition 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 this work, the shapes of liquid Pb and PbSn inclusions embedded in Al matrix were investigated by in-situ electron microscopy equipped with a video system. The aspect ratio of inclusions was measured from digitized micrographs using a 7-parameter least squares fit. It was found that the shapes of liquid inclusions depend on composition as well as size and temperature. Addition of Sn into Pb inclusions decreased not only the melting temperature of the inclusions but also the roughening transition temperature of Pb/Al interface. For pure Pb, the roughening transition temperature is about 550°C, while for PbSn inclusions, it was measured to be around 400°C. Our observations are discussed in terms of the effect of Sn on energy of steps in the interface between {111} Al and liquid Pb, and compared with previous reports on a wetting transition of liquid Sn at high angle grain boundaries in Al. This work was supported by the Director, Office of Science, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098, and the Danish Natural Sciences Research Council.

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TEM studies of plasticity mechanisms in nanocrystalline Ni during tensile deformation. Zhiwei Shan¹, Eric Stach², Jorg Wieszorek¹, Jim Knapp³, David Follstaedt³ and Scott Mao¹; ¹University of Pittsburgh, Pittsburgh, Pennsylvania; ²NCEM, Lawrence Berkeley National Laboratory, Berkeley, California; ³Physical and Chemical Science Center, Sandia National Laboratories, Albuquerque, New Mexico.

Mechanisms of plasticity active in nanocrystalline Ni during tensile

deformation have been studied by using different transmission electron microscope (TEM) observation modes. Both bright field and dark field observations revealed that grain boundary mediated processes contributed prominently to plastic deformation as predicted by theoretical consideration as well as molecular dynamics simulations. However, severe lattice distortions of grain interiors were detected by micro-beam electron diffraction (MBED). This apparently challenges the generally invoked assumption that interiors of nano-sized grains behave as a rigid body during deformation. Additionally, in situ high resolution TEM (HRTEM) observations have shown the presence of trapped lattice dislocations in grains still in a stressed state. Dynamics of the rearrangements of these dislocations during stress relaxation have been captured by HREM. A grain-size dependent model has been proposed to account for the experimentally observed phenomena.

4:00 PM P7.7

In-Situ Electron Microscopy Studies of the Effect of Solute Segregation on Grain Boundary Anisotropy and Mobility in Aluminum Alloys. Mitra L. Taheri¹, Anthony Rollett¹, Eric Stach² and Hasso Weiland³; ¹Materials Science and Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania; ²National Center for Electron Microscopy, Lawrence Berkeley National Laboratory, Berkeley, California; ³Alcoa Technical Center, Alcoa Center, Pennsylvania.

The presence of impurities in aluminum alloys is of great interest with respect to microstructural properties, specifically, the solute effect on texture and anisotropy. This paper presents new evidence of the pronounced effect of solute drag based on in-situ annealing and Electron BackScatter Diffraction experiments of solute-rich Al alloys subject to prior strain. In all alloy compositions studied, a compensation effect is noted in grain boundary mobility maxima for specific boundary types. A shift in axis-angle preference from $38-39^\circ \langle 111 \rangle$ to misorientation angles away from $40^\circ \langle 001 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$ is seen in alloys when annealed above the compensation temperature. In alloys with lower solute levels a faceting/defaceting transition is consistent with the boundary preference shift with increased temperature. Trends in activation energy binned by boundary type support the observations of a compensation effect with respect to solute and temperature. Evidence for irregular motion of boundaries from in-situ observations is discussed in reference to new theoretical results that suggest that boundaries migrating in the presence of solutes should move sporadically provided that the length scale at which observations are made is small enough. An in-depth study of both boundary motion and solute segregation to specific boundary types using Electron Energy Loss Spectroscopy with a Transmission Electron Microscope is presented.

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Formation and Growth of Epitaxial Cobalt Germanide Co₅Ge₇ Films Studied by in-situ Ultrahigh Vacuum Transmission Electron Microscopy. Xiaoqing Pan¹, Haiping Sun¹, Yanbin Chen¹, Dongzhi 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 germanides will be used as contact materials in the future Ge-based device. Compared with silicides that have been extensively investigated in the past, research on the formation of germanides 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 when Co is deposited. 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 involve different mechanisms for the two experiments mentioned. The identification of the Co₅Ge₇ phase by electron diffraction analysis will be discussed in detail.

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Self-limiting nano-oxidation of Cu₅₀at% Au alloy by in situ UHV-TEM. Liang Wang¹, Guangwen Zhou², Jeffrey A. Eastman² and Judith C. Yang¹; ¹Department of Materials Science and Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania;

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-assembly 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 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 (Cu_{0.5}Au_{0.5}) 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 grew with cube-on-cube crystallographical orientation to the Cu-Au film. This is attributed to greatly reduced strain energy in Cu₂O/ Cu_{0.5}Au_{0.5} 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.

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In Situ HREM Study on the Thermal Stability of

Self-Assembled InAs/GaAs Quantum Dots. Hyung Seok Kim¹,

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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.