

# SYMPOSIUM Q

## Advances in Materials Problem Solving with the Electron Microscope

November 30 – December 3, 1999

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\* Invited paper

SESSION Q1: MAGNETIC MATERIALS AND  
LOW-ENERGY ELECTRON MICROSCOPY

Chairs: Matthew R. Libera and Ivan Petrov

Tuesday Afternoon, November 30, 1999

Salon A/B (M)

**1:30 PM \*Q1.1**

**MAGNETISM, MICROSTRUCTURE AND MATERIALS CHARACTERIZATION WITH ELECTRON PROBES: ADVANCES AND APPLICATIONS.** Kannan M. Krishnan, Er. Girt, G. Kusinski and H.L. Ju, Materials Sciences Division, National Center for Electron Microscopy, Lawrence Berkeley National Laboratory, University of California, Berkeley, CA.

The key parameters defining the magnetic behavior of materials (coercivity, remanence, permeability and hysteresis loss) are essentially extrinsic properties that can be truly influenced by the microstructure. In atomically engineered thin films and nanostructures, much of the novel physical properties observed, such as perpendicular anisotropy and giant magnetoresistance, are due to the physical and chemical structure of the interfaces. In nanostructured materials, the coercivity and remanence can be tailored by controlling grain size/shape, defects, and most importantly, intergranular coupling and/or isolation. Hence, recent breakthroughs in magnetic materials follow from both advances in materials synthesis and the ability to characterize them by advanced electron-optical techniques at the appropriate length scales. Research in these areas will be described, drawing on recent examples, to illustrate the relationship between magnetism, microstructure and advanced TEM characterization methods. In particular, examples will include: (a) perpendicular anisotropy and inter-layer coupling in metallic heterostructures (b) tailored microstructures in hard magnet thin films and nanostructures (c) unusual substitution effects and description of the conductivity mechanism associated with the magnetotransport in manganite perovskites and (d) spin reorientations and domain structures in thin films with perpendicular anisotropy.

**2:00 PM Q1.2**

**ELECTRON HOLOGRAPHY OF NANOSTRUCTURED MAGNETIC MATERIALS.** R.E. Dunin-Borkowski, B. Kardynal, M.R. McCartney, M.R. Scheinfein, D.J. Smith, Center for Solid State Science, Center for Solid State Electronics Research, Dept. of Physics and Astronomy, Arizona State University, Tempe, AZ.

Off-axis electron holography provides access to the phase of the electron wave and hence the technique represents a powerful method for probing the magnetization within and surrounding magnetic materials. In this study, the magnetization behavior of nanostructured magnetic elements has been investigated using off-axis electron holography, and the results have been compared with micromagnetic simulations. Initial studies focussed on rectangular Co elements, and magnetic fields were applied to the samples in situ in order to determine the response of individual elements during hysteresis cycles. Observations exhibited switching asymmetries which were shown by simulations to be the result of strong inter-cell coupling as well as the residual field normal to the sample surface. The initial magnetization state also strongly influenced the magnetic domain configurations observed during field reversal. Further observations involved shaped elements resembling diamonds, ellipses and rectangular bars with emphasis placed on understanding the interlayer coupling within individual multilayered elements. It was concluded that the combination of experimental holographic measurements with micromagnetic simulations should enable unique insights to be obtained into fundamental micromagnetic behavior.

**2:15 PM \*Q1.3**

**STRUCTURE-PROPERTY STUDIES OF MAGNETIC THIN FILM MEDIA.** Robert Sinclair, Stanford University, Dept of Materials Science and Engineering, Stanford, CA.

Microstructural and micromagnetic characterization is important to understanding the magnetic performance of thinfilm, data storage materials. With cobalt alloy grain sizes typically in the range 10-20 nm, high-resolution imaging (or at least, very careful bright field) is essential for establishing the grain structure, average dimensions and size distributions quantitatively as a function of deposition conditions. Grain boundary segregation is an important parameter determining magnetic properties, which can be studied both by energy dispersive spectroscopy and by energy filtered imaging techniques. To correlate this information with the magnetic structure, Lorentz imaging methods are employed. The bittransition regions can be correlated with magnetic vortices in magnetically written thinfilms, and the demagnetized Lorentz structure depends strongly on the degree of magnetic decoupling of individual cobalt grains brought about by grain boundary segregation. The application of such electron

microscope experiments in this contemporary area of materials research will be demonstrated.

**2:45 PM Q1.4**

**MAGNETIC BEHAVIOR OF GRAIN BOUNDARIES IN Nd-Fe-B MAGNETS.** Viacheslav V. Volkoy, and Yimei Zhu, Dept. of Applied Science, Brookhaven National Laboratory, Upton, NY.

We present in-situ dynamic TEM observations on magnetic behavior of the grain boundaries (GB) in permanent Nd-Fe-B magnets prepared by different processing methods. The dynamic TEM observations in Fresnel imaging have been carried out using JEOL 2000FX and JOEL3000FEG microscopes under the free-lens-control mode with main objective lens either off or slightly exited to magnetize/ demagnetize the samples. Results of the experiments were recorded on videotapes. The advantages of the field emission gun (FEG) over the LaB<sub>6</sub>-cathode allowed us to realize a novel phase-coherent Foucault-imaging method [1] in studying dynamic interactions between magnetic domain walls and GBs. The magnetic interferograms produced by this method provide a quantitative description of the induction variation and are suitable for real-time observations. Both of Fresnel and phase-coherent Foucault imaging techniques have been successfully used to characterize the magnetic behavior of GBs in Nd-Fe-B permanent magnets. Our TEM observations suggest that the GBs play an important multi-functional role in the process of magnetization reversal, they may act as: (a) pinning centers, (b) centers of nucleation of reversal domains, (c) sink or source for migrating magnetostatic charges and/or dipoles. They also serve for smooth transient for irreversible magnetization in polycrystalline samples. The strength of the pinning centers, which is often associated with magnetic coupling or decoupling of grains, depends on the structure of the GB, i.e., GB thickness, composition as well as misorientation. Most of these features in magnetic properties and behavior of the GBs will be demonstrated in a video presentation. \* This work was supported by the U.S. Department of Energy, Division of Materials Science, Office of Basic Energy Science under the contract No. DE-AC02-98CH10886. Ref.: [1] A.B. Johnston, J.N. Chapman, B. Khamsehpour, and C.D.W. Wilkinson, J. Appl. Phys. 29 (1996) 1419-1427.

**3:30 PM \*Q1.5**

**BEYOND LEEM: SPLEEM AND SPELEEM.** Ernst Bauer, Thomas Duden, Department of Physics and Astronomy, Arizona State University, Tempe, AZ; Thomas Schmidt, ELETTRA, Trieste, ITALY.

LEEM is an imaging technique with slow electrons which gives information about the structure and topography of the surface via diffraction and interference contrast. For many purposes the chemical composition and bonding, the electronic and magnetic structure are also needed with high resolution. LEEM has been extended to magnetic imaging using a spin-polarized electron gun (SPLEEM) and to chemical and electronic imaging by combining LEEM with spectroscopic photoemission microscopy (SPELEEM) using synchrotron radiation for excitation. As a result, comprehensive surface analysis with high lateral and depth resolution is available now. Application examples from the fields of thin film magnetism and semiconductor surface physics will be presented.

**4:00 PM \*Q1.6**

**LOW ENERGY ELECTRON MICROSCOPY.** Ruud M. Tromp, IBM T.J. Watson Research Center, Yorktown Heights, NY.

Low Energy Electron Microscopy (LEEM) is one of the few electron microscopy methods that allow observation of a specimen inside the microscope to observe processes such as epitaxial growth, strain relaxation, interface formation, chemisorption and desorption, etcetera, in real time with videorate time resolution. The low electron energies used (typically below 50 eV) makes LEEM very surface sensitive, while at the same time minimizing beam-surface interactions. In this talk I will present recent results related to the growth of thin crystalline films, including SiGe alloys as well as semiconducting polymer films on Si substrates.

**4:30 PM \*Q1.7**

**LEEM STUDIES OF BCC REFRACTORY METAL HETERO-EPITAXY.** C.P. Flynn and W. Swiech, University of Illinois at Urbana-Champaign, Materials Research Laboratory, Urbana, IL.

We have devised methods that permit LEEM investigations of single crystal films grown on conducting or insulating substrates, and at temperatures up to 1700K. Here we describe studies of Mo (110) and Nb (110) grown 50-500 nm thick by molecular beam epitaxy on sapphire (11 $\bar{2}$ 0). By Low Energy Electron Microscopy (LEEM) we can observe evolution of structure at the interface, in the bulk and at the outer surface. In this contribution four critical aspects of thin film evolution are discussed: (1) The states passed through by surfaces

constrained to a specific vicinal miscut, under the influence of step-step interactions; this includes the important example of Nb (110) in which {110} facet formation dominates these interactions. (2) The evolution of bulk microstructure, including low angle grain boundaries, with the observed mobility of threading screw and edge dislocations and their release from pinning centers. (3) The time development of the interfacial epitaxial constraint, including slip from interfacial dislocations of various observed types and orientations. (4) Complex and newly observed interactions among these three categories of process, of which illustrative examples are (a) the way surface reconstructions interact with bulk epitaxial strains, with threading dislocations and with surface step edges; and (b) the direct interaction of surface features with the process of epitaxial strain relief proceeding through bulk slip at elevated temperatures.

## SESSION Q2: CRYSTALLOGRAPHY AND DEFECTS

Chairs: James Bentley and Kannan M. Krishnan

Wednesday Morning, December 1, 1999

Salon A/B (M)

### 8:30 AM \*Q2.1

**ELECTRON BACKSCATTER DIFFRACTION: A POWERFUL TOOL FOR PHASE IDENTIFICATION IN THE SEM.** J.R. Michael and R.P. Goehner, Sandia National Laboratories, Albuquerque, NM.

Electron backscatter diffraction (EBSD) is becoming a standard tool for the microstructural characterization of crystalline materials. One of the big disadvantages of SEM characterization has been the lack of a robust way to obtain crystallographic information about the specimen. The development of (EBSD) has overcome this disadvantage. The initial use of EBSD in the SEM was for the determination of texture of a sample related to some microstructural features. More recently EBSD has been applied to the identification of unknown micrometer and sub-micrometer phases in bulk samples, particles or on fracture surfaces. Phase identification has been accomplished in two ways. One method requires the user to provide a list of possible phases and then a simple comparison of crystallographic features is performed to determine which phase matches best. This technique has many limitations, the main one is that the user needs to have a good idea of what phases may be present. A second method uses the information from the pattern to calculate crystallographic parameters and then these are used along with the sample chemistry to search a data base for possible matches. This technique has a distinct advantage over the former method as there is no need to guess which phases may be present. This technique will be demonstrated in a variety of materials. Recent advances in the understanding of the information content of EBSD patterns may enable the Bravais lattice to be calculated directly from the patterns.

### 9:00 AM Q2.2

**RECONSTRUCTION OF A 3D MICROSTRUCTURE USING ORIENTATION IMAGING MICROSCOPY.** Wayne E. King, James S. Stölken, Adam J. Schwartz, Mark A. Wall and Lan Nguyen, Lawrence Livermore Natl Laboratory, Chemistry, Materials and Science Dept., Livermore, CA.

Orientation Imaging Microscopy (OIM) coupled with serial sectioning has been employed to acquire the necessary data to reconstruct in 3D the orientations and grain topologies in polycrystalline Ta. The average grain size of the material was  $\sim 40\mu\text{m}$ . OIM scans encompassed regions of dimension  $\sim 1200 \times 1200\mu\text{m}$  sampled over a hexagonal grid with  $4.5\mu\text{m}$  spacing. Data from forty-seven serial sections separated by  $4.9 \pm 1.2\mu\text{m}$  (Mark please enter this number) were acquired. In this manner overlapping data for about 1000 grains was obtained. The data from each section was aligned in orientation with an embedded Ta single crystal reference and spatially through cross correlation of the corrected orientation data from adjacent sections. The aligned data was then distributed in a 3D volume and interpolated such that both the orientation data and its derivative were continuous. The resultant volumetric data, known as the virtual test sample (VTS), is a complete digital representation of the orientation morphology that can be analyzed to study the topology of the microstructure and is amenable for transfer to finite element codes for simulation of plastic deformation. This work was performed at Lawrence Livermore National Laboratory under the auspices of the US Dept. of Energy under Contract W-7405-Eng-48.

### 9:15 AM Q2.3

**DETERMINATION OF THE THIN FILM STRAIN TENSOR FOR ALUMINUM GRAIN BOUNDARIES VIA A NEW IMAGE PROCESSING APPROACH TO CBED HOLZ PATTERNS.** Junya Inoue, Department of Civil Engineering, University of Tokyo, Tokyo, JAPAN; Alan F. Schwartzman, Lambert B. Freund, Division of Engineering, Brown University, Providence, RI.

HOLZ lines formed in a CBED pattern provide an accurate means to

measure a local strain tensor with very high spatial resolution over mesoscopic length scales. With the advent of energy-filtering in a field-emission TEM, the precision of this measurement increases by filtering out the inelastic scattered electrons. This paper presents an alternate approach to obtaining the same increased precision by image processing of CBED patterns formed in a conventional  $\text{LaB}_6$  microscope. This technique results in the determination of the full strain tensor within  $\pm 0.01\%$ . It is based on developing a Wiener filter for CBED patterns, deconvoluting the point spread function of the CCD camera, using the Hough transform to measure distances between HOLZ line intersections and subtracting out an experimentally determined projector lens distortion. Concurrently, for small uniform strains, theoretical simulations are performed to derive an  $n \times 7$  mapping function which determines how  $n$  HOLZ line intersection distances depend linearly on the six strain components and on the accelerating voltage. Once the accelerating voltage is experimentally calibrated using a perfect crystal and the HOLZ line intersection distances are measured, a least squares fit routine is applied to obtain the optimum set of strain components from the linear mapping function. This approach has been used to measure the strain tensor for the two types of grain boundaries found in MBE grown Al thin films on Si which have the mazed bicrystal microstructure.

### 9:30 AM \*Q2.4

**STUDIES OF GAS-SOLID INTERACTIONS IN A TRANSMISSION ELECTRON MICROSCOPE.** I.M. Robertson, Dept of Materials Science and Engineering, Urbana, IL.

A differentially pumped, double-aperture limited environmental cell has been installed in the objective pole-piece of a JEOL 4000 electron microscope. This arrangement allows a gaseous environment to be introduced into the microscope without adversely affecting the operation of the instrument. The availability of straining stages with temperature control from 100 to 1000 K and of a hot stage allows gas-solid interactions to be studied dynamically and at high spatial resolution under a wide range of experimental conditions. The basic design of the environmental cell will be described and its use illustrated by examples taken from our work on the effect of a gaseous hydrogen environment on the mechanical behavior of materials. The examples selected will show that hydrogen enhances the mobility of dislocations by an elastic shielding mechanism, reduces the stacking-fault energy of a material but not significantly, and prohibits cross-slip by stabilizing edge character dislocations. These results will be discussed in terms of current hydrogen embrittlement models.

### 10:30 AM \*Q2.5

**ALCHEMI ANALYSIS OF ATOMIC SITE DISTRIBUTIONS IN ORDERED ALUMINIDE INTERMETALLICS.** Ian M. Anderson, Lee M. Pike\* and Jim Bentley, Oak Ridge National Laboratory, Oak Ridge, TN; \*present address: Haynes International Inc., Kokomo, IN.

Atom-location by channeling-enhanced microanalysis (ALCHEMI) has emerged as a powerful tool for understanding the influence of alloying additions on the properties of ordered aluminate intermetallic alloys. Whereas early formulations of ALCHEMI yielded inaccurate and sometimes unphysical atomic site distributions for aluminate intermetallics, revised formulations now allow the extraction of accurate site distributions with standard errors smaller than 1% relative in favorable circumstances. This paper will review the factors influencing the accuracy of ALCHEMI, including the effects of ionization delocalization and anti-site defects, and will show how these factors are addressed in recent formulations of the technique. The results of extensive ALCHEMI measurements on B2-ordered aluminate alloys will then be used to illustrate trends in the site substitution behavior of ternary alloying additions as a function of the concentration of the alloying addition, its position in the periodic table, and alloy stoichiometry. These measurements will be used to show the relative influences of thermodynamic and kinetic factors during alloy processing and to explain the origin of physical and mechanical properties that depend upon these atomic site distributions. Research at the Oak Ridge National Laboratory SHaRE User Facility was sponsored by the Division of Materials Sciences, U.S. Department of Energy, under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corporation.

### 11:00 AM \*Q2.6

**A NOVEL QUANTITATIVE CBED TECHNIQUE FOR STUDYING CHARGE DISTRIBUTION IN COMPLEX OXIDES.** Yimei Zhu, Lijun Wu, J. Tafto Department of Applied Science, Brookhaven National Laboratory, Upton, NY.

Understanding the electronic structure of materials is crucial to understanding the behaviors of materials. To study property-determining valence-electrons distribution in superconductors, we developed a novel diffraction technique via Parallel Recording Of Diffraction Intensity (PARODI) as a function of

crystal thickness [1]. Through quantitative error analysis and refinement procedures we can determine Fourier components of the electron distribution in crystals with an accuracy ( $0.0003 \text{ electron} / \text{\AA}^{-3}$ ) that is far beyond previous achievements for crystals with large unit cells. This technique was applied to measure charge density normal to the a-b plane in YBCO and Bi/2212 superconductors, which was then converted to charge transfer using formal valences as a reference. The results were compared with the electronic structures based on first principle calculations. This technique was also applied to study charge segregation associated with crystal defects. Observations of charge ordering and charge stripes in nickelates and manganites will also be discussed. Work supported by the U.S. Department of Energy under Contract No. DE-AC02-98CH10886. [1] L. Wu, Y. Zhu and J. Taftø, Phys. Rev. B **59** 6035 (1999)

#### 11:30 AM Q2.7

ANALYSIS OF THE ATOMIC-SCALE DEFECT CHEMISTRY IN OXYGEN DEFICIENT MATERIALS BY SCANNING TRANSMISSION ELECTRON MICROSCOPY. Yasuo Ito, Susanne Stemmer, Nigel D. Browning, Univ of Illinois at Chicago, Dept of Physics, Chicago, IL; Ajit Sane, Terry J. Mazanec, BP Chemicals Inc, Cleveland, OH.

Anion-deficient perovskite type oxides often show a high mobility of oxygen vacancies at elevated temperatures and are therefore interesting for applications as electrodes in solid oxide fuel cells and potentially in oxygen separation membranes. Valence states of cations and ordering of anion vacancies affect the performance of the devices. As model oxygen-deficient oxides, we have investigated two types of oxygen-deficient strontium cobaltites, hexagonal ( $\text{Sr}_6\text{Co}_5\text{O}_{15}$ ) and a perovskite  $\text{SrCoO}_{3-x}$ . The perovskite sample was stabilized by cyclic heat treatments in reducing and oxidizing atmospheres. Unlike the hexagonal sample, the perovskite sample is found to consist of ordered microdomains. Furthermore, preliminary Z-contrast images from the perovskite material indicate that the ordering occurs with point defects being located in every second cobalt-oxygen plane. To further investigate the valence states of cobalt and the possible ordering of cation/oxygen vacancies, electron energy-loss spectroscopy was used in conjunction with the Z-contrast imaging technique. Using this analysis, the valence states of cobalt were determined by quantifying the cobalt  $L_{2,3}$ -edges ( $L_3/L_2$  ratio). The preliminary results show that the valence state of the hexagonal sample (3.0-3.5) agrees with the reported literature values (3.6) and the valence state of the perovskite sample is reduced to 2.5. Complimentary information on changes in the coordination of the cations to the surrounding oxygen, i.e. tetrahedral or octahedral, due to the presence of oxygen vacancies can be obtained from the oxygen K-edge. Multiple-scattering simulations of the oxygen K-edge fine structure are consistent with these experimental observations.

#### 11:45 AM Q2.8

ENERGY DISPERSIVE X-RAY SPECTROMETRY WITH THE TRANSITION EDGE SENSOR MICROCALORIMETER: A REVOLUTIONARY ADVANCE IN MATERIALS MICROANALYSIS. Dale Newbury, David Wollman, Kent Irwin, Gene Hilton, John Martinis, National Institute of Standards and Technology, Gaithersburg, MD and Boulder, CO.

X-ray microanalysis currently relies on the semiconductor energy dispersive spectrometer (EDS), which provides a complete view of the spectrum but with only modest resolution (e.g., 130 eV at Mn K-alpha), and/or the wavelength dispersive spectrometer (WDS), which provides high spectral resolution (8 eV at Mn K-alpha) at the cost of mechanical scanning (with several diffractors) to view the spectrum. The Transition Edge Sensor Microcalorimeter EDS recently developed by NIST combines high resolution (8 eV at Mn K-alpha) and energy dispersive operation (photon energy range from 250 eV to 10 keV). Moreover, for the photon energy range from 250 eV to 2 keV, resolution of 3 eV or less can now be achieved, enabling studies of 'chemical shifts', that is changes in x-ray peak position, shape, and relative yield due to chemical bonding effects. While the microcalorimeter EDS will provide important benefits for all electron-excited x-ray spectrometry techniques, such as electron probe microanalysis at conventional beam energies (10 - 30 keV) and analytical electron microscopy at high beam energies (100 - 400 keV), the microcalorimeter EDS is critical for materials problem solving with low voltage (beam < 5 kV) microscopy (LVSEM). As performed in the field emission gun scanning electron microscope (FEGSEM), LVSEM offers high spatial resolution of 100 nm or less. However, operation at low beam energy limits access to atomic shells, forcing selection of L, M, and N shells which may have only limited fluorescence yields. The high peak-to-background ratio achievable with the TES microcalorimeter enables detection of many peaks that cannot be measured by semiconductor EDS, especially in the C - O portion of the spectrum (200 - 600 eV). Applications of LVSEM/TES microcalorimeter EDS to compounds such as barium titanate, titanium nitride, and tungsten silicide will illustrate these new capabilities.

### SESSION Q3: MICROELECTRONIC MATERIALS

Chairs: Joseph R. Michael and Robert Sinclair

Wednesday Afternoon, December 1, 1999

Salon A/B (M)

#### 1:30 PM Q3.1

MEDIUM RANGE STRUCTURE OF AMORPHOUS SEMICONDUCTORS REVEALED BY FLUCTUATION MICROSCOPY. P.M. Voyles, University of Illinois, Dept. of Physics, Urbana, IL and NEC Research Institute Inc., Princeton, NJ; J.M. Gibson, Argonne National Laboratory, Argonne, IL; M.M.J. Treacy, NEC Research Institute Inc., Princeton, NJ.

Fluctuation microscopy is a new technique for garnering information about medium range structure in disordered materials with the electron microscope. A low-resolution dark-field micrograph can be viewed as a map of the diffracted intensity variations from mesoscopic volumes. Quantitative statistical analysis of that map yields a function which depends on the four-body pair-pair atomic correlation function. The four-body correlation function has greater sensitivity to medium range structure than the two-body correlation function available from diffraction, as shown by calculations from molecular dynamics model structures. We have measured significant medium range order in tetrahedral amorphous semiconductors at a length scale of  $\sim 1.5 \text{ nm}$ , which has led us to the paracrystalline model for their structure [M. M. J. Treacy, J. M. Gibson, and P. J. Kebabian, J. Non-Cryst. Solids **231** 99 (1998)]. This structure is present in amorphous thin films of various materials, including Ge, Si, and hydrogenated Si, deposited by a variety of techniques, including evaporation, reactive sputtering, and plasma enhanced and hot-wire chemical vapor deposition. Thermal annealing reduces this medium-range order to levels typical of a continuous random network. Light exposure produces a similar reduction in hydrogenated amorphous Si, which may have implications for the Staebler-Wronski effect. Results from fluctuation microscopy correlate with Raman spectroscopy measurements of medium-range order.

#### 1:45 PM \*Q3.2

IN-SITU TEM APPLICATION OF THERMAL, MECHANICAL, ELECTRICAL AND OPTICAL STRESSES TO DISLOCATIONS IN SEMICONDUCTOR HETEROSTRUCTURES. Robert Hull, Department of Materials Science and Engineering, University of Virginia, Charlottesville, VA.

Atomic-scale control of growth of semiconductor heterostructures has enabled development of broad new classes of microelectronic and optoelectronic devices, such as semiconductor laser diodes, heterojunction bipolar transistors and modulation doped field effect transistors. Integration of materials with different lattice parameters, however, raises the issue of strain-relieving interfacial dislocation arrays, known as misfit dislocations. The energetics and kinetics of generation of misfit dislocation arrays is thus a critical issue in the growth and processing of lattice-mismatched heterostructures. In this presentation, we will describe in-situ TEM observations that provide detailed insight into the energetics, kinetics of formation, and properties of the misfit dislocation array. Extensive results have been obtained for the GeSi/Si, GeSi/Ge, InGaAs/GaAs and InGaAs/InP (100), (110) and (111) systems. A range of sample holders has been constructed which enables in-situ application of thermal, mechanical, electrical and optical stresses to the sample. Application of thermal and/or mechanical stresses allows dislocation nucleation, propagation and interaction processes to be directly observed and quantified. We will show that these measurements may be integrated into a predictive simulator that we have developed for plastic strain relief in heteroepitaxy. In-situ application of electrical and optical stresses enables carrier- and photon-induced degradation modes to be studied, as well as fundamental electrical properties of the dislocations to be measured. This research is done in collaboration with J. Bean, J. Demarest, D. Dunn, D. Mathes and Q. Yuan (U. Virginia), E. Stach (LBL) and M. Reuter, F. Ross and R. Tromp (IBM)

#### 2:15 PM \*Q3.3

GROWTH AND CHARACTERIZATION OF HETEROEPITAXIAL SYSTEMS - SOME RECENT DEVELOPMENTS. David J. Smith, Center for Solid State Science and Dept. of Physics and Astronomy, Arizona State University, Tempe, AZ.

There are many ongoing challenges associated with the fabrication of heterostructures based on two (or more) dissimilar materials. In addition to lattice mismatch, which inevitably leads to strain and possible defect formation, valence mismatch and differences in thermal expansion, are factors that can seriously impact whether or not high quality materials can be grown. Microstructural characterization and close interaction with the crystal grower plays a valuable role in

understanding and optimizing materials properties. This talk will concentrate on three systems of much current scientific and industrial interest: a) heterostructures based on SiGeC/Si, which offer the intriguing prospect of band-gap engineering in a lattice-matched system; b) CdTe/Si substrates, which allow the monolithic integration of Si electronics with MCT (mercury cadmium telluride) infrared detectors; and c) alloys of Group III-nitrides, which promise to totally revolutionize the microelectronics and optoelectronics industries.

#### 2:45 PM Q3.4

STRAIN PROFILING OF GaN/Al<sub>x</sub>Ga<sub>1-x</sub>/In<sub>y</sub>Ga<sub>1-y</sub>N HETEROSTRUCTURES BY ELECTRON HOLOGRAPHY. Y.C. Wang, FEI Company, Hillsboro, OR; C. Kisielowski, E.C. Nelson, C. Song, NCEM, Lawrence Berkeley National Laboratory, Berkeley, CA.

Strain in GaN/AlN/InGaN based thin-film heterostructures originates from a large lattice mismatch between the matrix and the buried layers. The strain will give rise to local piezoelectric fields in these polar materials. Electron holography enables us to extract compositional profiles and electric fields across GaN/Al<sub>x</sub>Ga<sub>1-x</sub>N and GaN/In<sub>y</sub>Ga<sub>1-y</sub>N quantum wells. In addition, electron holograms recorded on the [11 $\bar{2}$ 0] zone-axis of GaN/Al<sub>x</sub>Ga<sub>1-x</sub>/In<sub>y</sub>Ga<sub>1-y</sub>N device structures also allow a simultaneous recording of lattice images. Therefore, the phase and amplitude information of the hologram can be compared with quantitative and local strain measurements deduced from lattice images. Dynamical scattering is unavoidable when recording the holograms on the zone-axis. We have tilted the GaN/Al<sub>x</sub>Ga<sub>1-x</sub>/In<sub>y</sub>Ga<sub>1-y</sub>N samples away from the zone-axis to minimize the dynamical scattering effect. A phase shift of  $\sim 2$  radian across the GaN/Al<sub>x</sub>Ga<sub>1-x</sub>N and GaN/In<sub>y</sub>Ga<sub>1-y</sub>N quantum wells was observed on a nanometer scale before and after tilting away from the zone-axis. This observed phase shift across GaN/Al<sub>x</sub>Ga<sub>1-x</sub>/In<sub>y</sub>Ga<sub>1-y</sub>N heterostructures must be influenced by the presence of the p-n junction in the device, by compositional changes and by the piezoelectric field. The individual contributions of these effects to the overall phase change will be discussed.

#### 3:30 PM Q3.5

MICRODIFFRACTION, CBED, AND HREM FOR PHASE IDENTIFICATION AND ATOMIC STRUCTURE ANALYSIS OF CRYSTALLOGRAPHIC DEFECTS. Pierre Ruterana, Gerard Nouet, Laboratoire d'Etudes et de Recherches sur les Matériaux, UPRESA CNRS 6004, ISMRA, Caen, FRANCE; Philippe Vermaut, Laboratoire de Metallurgie Structurale, Ecole Supérieure de Chimie de Paris, Paris, FRANCE; Abdel Redjaomia, Laboratoire de Science et Genie des Surfaces, CNRS, Ecole des Mines, Nancy, FRANCE; Jean-Paul Morniroli, EUDIL, Villeneuve d'Ascq, FRANCE; Anna Vila, Departament d'Electronica, Universitat de Barcelona, Barcelona, SPAIN; Marc Loubradon and Roland Bonnet, Institut National Polytechnique de Grenoble, LTPCM, Saint-Martin d'Herès, FRANCE.

The techniques of electron microscopy have been used in order to identify nanophase either individually or by combination. For macro or nanophase identification no other possibility than electron microscopy exists and one has to use two or three methods at least in order to completely solve the problem. In this contribution it will be shown that the microdiffraction method which uses a very small diameter parallel beam allows to determine the complete local symmetry and a case study will be presented in an austenite stainless steel where a new phase was recently completely determined by combining this method with quantitative EDS and HREM. The fine use of CBED has now proven to be very powerful in determining the polarity in important materials in our work it was possible to solve completely such problems in AlN/GaN layers grown on SiC or sapphire where closed domains form as stacking fault or inversion domains. Such domains were clearly shown to be stacking faults on top of SiC by a careful combinations of CBED and HREM. Conventional high resolution microscopy is still a very good method for analysing the core structure of important crystallographic defects such as dislocations and stacking faults. In this case a combination of modelling and image interpretation has proven to lead to non-ambiguous results. Case studies are discussed for the strain relaxation at the GaAs interface and formation of prismatic faults in GaN thin films.

#### 3:45 PM Q3.6

STEM BASED MEASUREMENTS OF LATERAL COMPOSITION MODULATION IN InAlAs FILMS. R.D. Twisten, University of Illinois, Urbana, IL; D.M. Follstaedt, S.R. Lee, E.D. Jones, J.L. Reno, Sandia National Laboratories, Albuquerque, NM; J. Mirecki Millunchick, University of Michigan, Ann Arbor, MI; A.G. Norman, S.P. Ahrenkiel, A. Mascarenhas, National Renewable Energy Laboratory, Golden, CO.

One goal of current research in optoelectronic device fabrication is to form structures that exhibit two- and three-dimensional quantum confinement to enhance device performance. A method of forming

such structures is through the spontaneous lateral modulation seen in MBE grown short-period superlattices (SPS) of III/V materials. We have analyzed films consisting of InAs/AlAs SPS (superlattice period  $\sim 4$  monolayers) grown on InP substrates under a range of conditions. Electron based microcharacterization has proven to be a powerful tool in understanding these modulated films. Here we report the results of nanometer scale characterization of the composition distribution within these films using scanning transmission electron imaging and microanalysis. We find that combining high-angle annular dark-field (HAADF) imaging with characteristic x-ray (EDS) analysis, the details of the modulation can be observed. In particular for samples grown under slight tension ( $\sim 0.4\%$ ) with respect to the InP substrate, EDS analysis reveals an InAs enrichment of 0.23 mole fraction but only a 0.15 InAs mole fraction depletion in the AlAs rich regions. HAADF imaging reveals this is the result of an asymmetric modulation profile consisting of sharply peaked InAs rich regions ( $\sim 4$ nm wide) separated by broad regions of AlAs rich material ( $\sim 10$ nm wide). This degree of In enrichment is consistent with the red shift observed in our photoemission data as well. HAADF imaging also reveals presence of interlayer mixing of the SPS layers during growth. This intermixing will modify the interlayer strain energy which is expected to be a high energy component of the system. A portion of this work was performed at the Center for Microanalysis of Materials which is supported by U.S. DOE grant DE-FG02-91ER45439. The authors acknowledge the support of the U.S. DOE, OER/BES Division of Materials Science grant DE-AC02-83-CH10093, and support for Sandia National Laboratories by the U.S. DOE contract DE-AC04-94AL85000.

#### 4:00 PM Q3.7

ENERGY-LOSS FILTERED IMAGING OF SEGREGATION-INDUCED INTERFACE BROADENING IN SiGe/Si p-CHANNEL MOSFET DEVICE STRUCTURES. D.J. Norris, A.G. Cullis, Dept. of Electronic and Electrical Engineering, University of Sheffield, Sheffield, UNITED KINGDOM; T.J. Grasby, E.H.C. Parker, Dept. of Physics, University of Warwick, Coventry, UNITED KINGDOM.

The demand for increasingly high-speed analogue and digital electronics has prompted a drive for a more advanced Si-based device technology. Such devices as the p-channel SiGe/Si FET, required for CMOS device circuitry, have been found to give much improved hole mobilities compared with conventional Si-based devices. This derives, in particular, from the modification of the band structure owing to pseudomorphic straining of the alloy channel; however, the approach relies heavily on producing uniform SiGe layers with highly abrupt interfaces. Interface sharpness is not easy to control and, therefore, it is crucial to analyse the SiGe channel on the nano-scale to determine the finest details of composition gradations. Chemical profiles across such layers obtained from convention two-beam TEM images are often non-quantitative due to the presence of addition strain contrast. Consequently, Ge composition profiles across MBE-grown SiGe channels, in this study, have been determined on the nanometre scale using advanced energy-loss filtering in the field emission gun TEM: both electron energy-loss spectroscopy and filtered imaging have been employed. In this paper, we will show that the distribution of Ge across the channel interfaces is asymmetrical due to the effects of segregation during growth. A quantitative comparison will be made between these composition measurements, corresponding SIMS studies of similar samples, and the predictions of theoretical models of the segregation phenomenon.

#### 4:15 PM Q3.8

ATOMIC-SCALE IMAGING OF DOPANT ATOMS DISTRIBUTIONS WITHIN SILICON  $\delta$ -DOPED LAYERS. D.A. Muller, H.J. Gossmann, P.H. Citrin, Bell Labs, Lucent Technologies, Murray Hill, NJ; R. Vanfleet, J. Silcox, School of Applied and Engineering Physics, Cornell University, Ithaca, NY.

We report measurements of the distribution of Sb atoms in  $\delta$ -doped Si, over a wide 2-D concentration range. Both annular dark-field imaging and electron energy loss spectroscopy proved sufficiently sensitive to locate Sb atoms at the atomic scale. Improvements in both detector sensitivities and specimen preparation were necessary to achieve these results, which offer a surprising explanation for the dramatic difference in electrical activity between 2-D and 3-D dopant distributions at the same effective volume concentrations. The prospects for the general identification of individual dopant atoms will be discussed.

#### 4:30 PM Q3.9

PEEM IMAGING OF DOPANT-CONTRAST IN Si DEVICES. V.W. Ballarotto, K. Siegrist, R.J. Phaneuf, E.D. Williams, University of Maryland, Dept. of Physics, College Park, MD.

One of several possible contrast mechanisms in Photoelectron Emission Microscopy (PEEM) is local variation of photothreshold [1]. In silicon, the effective photothreshold can be reduced by degenerate

doping [2]. Intentional spatial variation of doping, such as in a pn junction, produces contrast in PEEM that may be useful for dopant profiling. By imaging a lateral array of silicon pn junctions with PEEM, spatially resolved information on doping has been achieved. Device structures were fabricated using standard photolithography and Focused Ion Beam (FIB) writing. The devices consisted of p-type stripes of various dopant concentrations ( $10^{18}$ - $10^{20}$  cm<sup>-3</sup>) and line separations written on n-type ( $10^{14}$  cm<sup>-3</sup>) Si (100) substrates. We find that the image intensity from the p-type region increases with doping. We measure a relative ratio of the p-stripe intensity to the n-type intensity of 8:4:1.5 for p-doping of  $10^{20}$ ,  $10^{19}$ ,  $10^{18}$  cm<sup>-3</sup>. We have done a quantitative characterization of the devices including extraction of line-widths which we compare with topographical features in AFM micrographs. We also assess the signal-to-noise and instrument-response available in the pn junction PEEM images. Work supported by Laboratory for Physical Sciences and the University of Maryland NSF-MRSEC. [1] M. Giesen, R.J. Phaneuf, E.D. Williams, T.L. Einstein and H. Ibach, Appl. Phys. A-Mater. 64, 423, (1997). [2] F.G. Allen and G.W. Gobeli, Phys. Rev. 127, 150, (1962).

#### 4:45 PM Q3.10

IN-SITU ANNEALING TRANSMISSION ELECTRON MICROSCOPY (TEM) STUDY OF THE Pd/Ge/Pd/GaAs INTERFACIAL REACTIONS. F. Radulescu, J.M. McCarthy, Oregon Graduate Institute of Science and Technology, Dept. of Materials Science and Engineering, Portland, OR; E.A. Stach, Lawrence Berkeley National Laboratory, National Center for Electron Microscopy, Berkeley, CA.

In-situ TEM annealing experiments on the Pd (20 nm) / a-Ge (150 nm) / Pd (50 nm) / GaAs ohmic contact system have permitted real time determination of the evolution of contact microstructure. As-deposited cross-sectional samples of equal thickness were prepared by using a focused ion beam (FIB) method and then were subjected to in-situ annealing at temperatures between 130-400°C. Excluding Pd-GaAs interactions, four sequential solid state reactions were observed during annealing of the Pd:Ge thin films. First, interdiffusion of the Pd and Ge layers occurred, followed by formation of the hexagonal Pd<sub>2</sub>Ge phase. This hexagonal phase then transformed into orthorhombic PdGe followed by solid state epitaxial growth of Ge at the contact / GaAs interface. The kinetics of the solid state reactions, which occur during ohmic contact formation, were determined by measuring the grain growth rates associated with each phase from the videotape observations. This data agreed with a previous study that measured the activation energies through a differential scanning calorimetry (DSC) method. We established that the Ge transport to the GaAs interface was dependent upon the grain size of the PdGe phase. The nucleation and growth of this phase was demonstrated to have a significant effect on the solid phase epitaxial growth of Ge on GaAs. These findings allowed us to engineer an improved two step annealing procedure that would control the shape and size of the PdGe grains. Based on these results, we have established the suitability of combining FIB for sample preparation with in-situ cross-sectional TEM annealing for studying thin film solid-state reactions.

#### SESSION Q4: POSTER SESSION: DEFECTS AND CRYSTALLOGRAPHY

Chairs: Vinayak P. Dravid, Ian M. Robertson and  
Andreas Thust

Wednesday Evening, December 1, 1999  
8:00 P.M.

Exhibition Hall D (H)

#### Q4.1

SLIP PROPAGATION AND SLIP-STEPS INTERACTIONS STUDIED BY LEEM. W. Swiech, M. Mundschauf and C. P. Flynn, Materials Research Laboratory and Physics Department, University of Illinois at Urbana-Champaign, Urbana, IL.

We report observations of slip processes in epitaxial films of Mo(110) grown on sapphire (11 $\bar{2}$ 0) by molecular beam epitaxy. Low-energy electron microscopy (LEEM) is employed to follow the time evolution of the screw dislocation, the interfacial dislocation, and the surface step edge structure, through which the slip takes place. Under certain conditions the dislocation system is observed to trap briefly as it meets successive surface steps. Surface steps and slip traces at surfaces are imaged through interference contrast (geometrical phase contrast) whereas defects at buried interfaces are visible through the strain fields they cause at the front surface. Other examples will be described in which structural defects influence surface microtopography. These include propagation of buried interfacial dislocations, annihilation of interfacial dislocations with slip trace formation, terrace coalescence, migration of edge dislocations, and dragging of atomic steps.

#### Q4.2

SURFACE SENSITIVITY EFFECTS WITH LOCAL PROBE SCANNING AUGER-SCANNING ELECTRON MICROSCOPY.

D.T.L. van Agterveld, G. Palasantzas, J.Th.M. De Hosson, Department of Applied Physics, Materials Science Center and Netherlands Institute for Metals Research, University of Groningen, Groningen, THE NETHERLANDS.

So far, experimental studies have shown that the surface topology may have a substantial influence in depth resolution during depth profiling in scanning Auger-scanning electron microscopy. However, because up to now finite beam sizes of the order  $\sim 0.1$ -1 mm (or larger) were commonly used, precise quantification of topology effects were rather limited. Only recently, the introduction of field emission electron guns with nanometer beam spot sizes ( $\sim 10$ -20 nm) opens the possibility for nanometer scale quantification of roughness effects. This paper outlines a possible methodology and summarizes some results obtained. The nanometer lateral electron probe size of the order of 10 nm yielded peak-line profiles that capture surface topology variations down to nanometer length scales. Surface roughness leads to peak intensity fluctuations which are described within the weak roughness limit by a simple form  $I(r) = (1+bh(r))$ ,  $h(r)$  represents the roughness fluctuation along a lateral in-planar distance  $r$ , and  $b$  is a constant. In addition, analyses of the peak-difference correlation function showed a power law behavior, with the power ranging between 0.7 and 1 at small length scales, i.e. for  $r$  smaller than  $x$ , with  $x$  a peak correlation length that was comparable to average specimen cluster sizes. Experimental observations are presented for pure Al and a eutectic Al-Mg alloy.

#### Q4.3

LOW-VOLTAGE EDS SPECTRUM-IMAGING OF METALS, CERAMICS AND SEMICONDUCTORS. Ian M. Anderson, Oak Ridge National Laboratory, Oak Ridge, TN.

X-ray microanalysis of bulk specimens at low ( $\leq 5$  kV) operating voltages can lead to an order of magnitude improvement in spatial resolution relative to the approximately one micrometer resolution achievable at conventional (15 - 30 kV) operating voltages in the scanning electron microscope or the electron probe microanalyzer. Spectrum-imaging, where a full spectrum is acquired for each pixel in a two-dimensional array, provides a comprehensive method for characterizing a specimen, as long as the pixel spacing is sufficiently smaller than the spatial resolution. Low-voltage energy-dispersive X-ray spectrometry (EDS) spectrum imaging combines the advantages of these two methods to provide high-spatial resolution ( $\leq 250$  nm) chemical maps of a specimen microstructure. Low-voltage EDS spectrum-images of a variety of metal, ceramic and semiconductor specimens will be presented to illustrate the power and unique benefits of this technique for materials characterization. The use of multivariate statistical analysis (MSA) for extracting the significant microchemical components from the large (typically  $>10$  MByte) raw data files will also be discussed. Research at the Oak Ridge National Laboratory SHaRE User Facility was sponsored by the Division of Materials Sciences, U.S. Department of Energy, under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corporation.

#### Q4.4

ELEMENTAL MAPPING OF STEELS CONTAINING NiCrMoV. Adam J. Papworth, David B. Williams, Lehigh University, Materials Research Center, Whitaker Laboratory, Bethlehem, PA.

Steels used in steam turbine applications are susceptible to temper embrittlement if operated at temperatures above 400°C. The cause of this embrittlement is the segregation of impurity elements, mainly phosphorus, to the prior austenite grain boundaries. Molybdenum can act as an effective scavenger for phosphorus, but the scavenging effect is lost when the molybdenum is precipitated in carbides during service at these elevated temperatures. Thus, the very slow temper embrittlement is controlled by the rates of alloy carbide formation, rather than by the diffusion of phosphorus, for example. The presence of vanadium apparently retards the embrittlement process even more by interfering with the formation of the molybdenum-rich carbides. Vanadium carbonitrides, are small, only a few nanometers in size. Analysis requiring the detection of these precipitates presents problems, as they can not be detected by either the annular dark field or bright field detector. Elemental X-rays maps can detect these small precipitates, but take time to acquire, therefore, have low statistics. M. Watanabe et al<sup>1</sup> has implied that with the use of the  $\zeta$  factor method, X-ray maps can be quantified but requires the background to be removed. This limits this approach to systems that have their X-ray peaks well spaced and without any conflicts. Steels consist of many elements, which have conflicts in their X-ray peaks. To quantify these elements the X-ray peak would have to be deconvoluted from each other, which is not possible at this moment. It is important to find concentrations of the elements, such as vanadium for example,

with its association with molybdenum and the formation of carbides or carbonitrides. A simple method of determining the qualitative concentrations has been developed and has proved to be surprisingly accurate.

<sup>1</sup>M. Watanabe, Z. Horita, M. Nemoto, *Ultramicroscopy* 65 (1996) 187-198.

#### Q4.5

**EMPIRICAL IDENTIFICATION OF URANIUM OXIDES USING EELS.** Stephen Rice, Hazel Bales, John Roth, Allen Whiteside, McCrone Associates, Inc., Westmont, IL.

Uranium compounds relevant to contaminated soils were studied by electron energy loss spectroscopy (EELS). Core-loss EELS results suggest that uranium 4<sup>+</sup> compounds have an energy loss resolvable from 6<sup>+</sup> compounds. Low-loss characteristics distinguish carbon-free uranium oxide specimens on holey substrates. In the presence of carbon, correction techniques must be applied. Uranium oxides, fluorides and minerals show a tendency toward reduction of uranium under the electron beam. The conditions for low-loss analysis need not be as vigorous as those for core-losses, and can be carried out without altering the valence of most oxides.

#### Q4.6

**A STUDY OF ALPHA- AND BETA- NICKEL SULFIDE BY HIGH RESOLUTION TEM.** John C. Barry, Centre for Microscopy and Microanalysis, The University of Queensland, Brisbane, Queensland, AUSTRALIA.

Nickel sulfide (NiS) is an important nickel bearing ore, and the high temperature hexagonal (alpha) form of NiS has unusual electronic and magnetic properties. However, in this work we are interested in the association of NiS with the spontaneous fracture of toughened glass, where the NiS inclusion is found on a fracture surface at the initiation-of-fracture point. Fracture of toughened glass occurs when NiS inclusions in the hexagonal (alpha) state transform within the glass to the rhombohedral (beta) state, which leads to an expansion of 4%. It is the phase transformation expansion of the inclusion which fractures the glass. In this work we liberate the NiS inclusion from the surface of a fracture die by dissolving the surrounding glass matrix with hydrofluoric acid. The inclusion is mounted into a 3 mm slot grid with epoxy. The sample is then ground, dimpled, and ion milled to electron transparency. Transmission electron microscopy (TEM) of the NiS inclusions reveals that they are polycrystalline. The larger of the crystal grains are in the beta form (they have transformed), but many of the smaller grains remain in the alpha (untransformed) state. There were problems in attempting to match simulated and experimental images of beta NiS. There is qualitative agreement but an asymmetry exists in the experimental image that is not reproduced in the simulation. The differences could be an indication of remanent strain in the transformed grains or it may be that high resolution TEM images are very sensitive to crystal misalignment.

#### Q4.7

**ORIENTATION IMAGING OF LOW ANGLE MICROSTRUCTURES: APPLICATION OF RODRIGUES-FRANK MAPPING.** Krishna Rajan, Materials Science and Engineering Dept., Rensselaer Polytechnic Institute, Troy, NY.

With developments in hardware and data processing, the technique of orientation mapping using electron diffraction techniques (such as EBSP) has become very popular. The full value of such techniques however require that there is enough resolution to detect the varying levels of misorientation that may occur within the microstructure. This is of particular importance in dealing with low angle microstructures. In this paper we show how Rodrigues-Frank representations of misorientation provide a far greater level of sensitivity in orientation imaging than is presently used. The analytical framework for developing such representations and the value of incorporating such formulations into orientation imaging is discussed.

#### Q4.8

**STRAIN ANALYSIS WITH LARGE-ANGLE CBED.** Helge Heinrich, Alessandro Vanati, Gernot Kostorz, ETH Zürich, Institute of Applied Physics, Zürich, SWITZERLAND.

Large-angle convergent beam electron diffraction (LACBED) images of short-fiber reinforced Al-based metal matrix composites indicate the presence of stresses in Si grains and in Al grains near the fibers. The experimental images are compared with dynamical many-beam LACBED simulations of distorted crystals. While high stresses are present in Si grains, dislocations reduce the strain fields near fibers in Al grains. Deformation twins in the  $\gamma$ -phase of lamellar two-phase TiAl/Ti<sub>3</sub>Al induce high stresses in neighboring  $\alpha_2$  lamellae. With two weak-beam images of an  $\alpha_2$  lamella, one component of the resulting

strain field can be evaluated quantitatively. The strain fields are compared with data obtained from LACBED. If the  $\alpha_2$  lamellae exceed a thickness of about 200 nm, they efficiently shield the stress fields induced by the deformation twins in the  $\gamma$  phase.

#### Q4.9

**HIGH SENSITIVITY CONVERGENT BEAM ELECTRON DIFFRACTION FOR THE DETERMINATION OF THE TETRAGONAL DISTORTION OF EPITAXIAL FILMS.** Carsten Schuer, Markus Leicht, Tamas Marek and Horst P. Strunk, Institute for Microcharacterisation, Friedrich-Alexander-University Erlangen-Nuremberg, GERMANY.

The advantage of convergent beam electron diffraction (CBED) for the determination of the lattice distortion of epitaxial films is its high spatial resolution of typically 10nm. However, the sensitivity to lattice distortion usually achieved by CBED is 0.2% and limited theoretically to 0.02% [1]. On the other hand, high resolution x-ray diffraction (HR-XRD) offers a higher sensitivity to lattice parameter changes, but its results are usually averaged over several micrometers of film thickness. Our aim is to determine with high spatial resolution the tetragonal distortion of GaAs epitaxial layers which were grown at reduced substrate temperatures of about 200°C by molecular beam epitaxy (MBE). One structural feature of this 'low temperature grown' (LT-) GaAs material is an increased lattice constant in growth direction (c-axis) of up to  $\Delta c/c = 0.13\%$ . This is correlated with an excess As content [2] of up to 1.5%. We optimize the sensitivity of CBED by orienting the sample such that the central (000) diffraction disc shows a pattern of defect lines most sensitive to tetragonal distortion. Furthermore we compare the position of these lines in the experimentally obtained images with results from computer simulations, which rely on the theory of dynamical diffraction. The positions of the defect lines are determined by applying the Hough transform to experimental and simulated images. Using this procedure, we can measure the tetragonal distortion of an LT-GaAs layer as low as 0.04%. We plan to apply this method to measure the As distribution in LT-GaAs layers and the strain field around As precipitates in annealed LT-GaAs. References: [1] D.B. Williams, C.B. Carter; *Transmission Electron Microscopy, Vol. 2 Diffraction*; Plenum, New York (1996) [2] X. Liu, A. Prasad, J. Nishio, E.R. Weber, Z. Liliental-Weber, W. Walukiewicz; *Appl. Phys. Lett.* 67 (1995) 279

#### Q4.10

**DETERMINATION OF COHERENCY STRAIN FIELDS AROUND COHERENT PARTICLES IN Ni-Al ALLOYS BY HREM AND CBED.** H.A. Calderon, J.J. Cruz, L. Calzado, Instituto Politecnico Nacional, Mexico D.F, MEXICO; C. Kisielowski, C.Y. Wang, R. Kilaas, NCEM-LBNL, Berkeley CA.

Quantitative evaluation of coherency strains around particles in the alloy Ni-12 at.%Al has been performed by means of high resolution electron microscopy (HREM) and convergent beam electron diffraction (CBED). Evaluation of the elastic strain fields around particles can give insight into the elastic interaction between particles during their coarsening mechanism and especially for the late stages where the elastic energy becomes particularly important. Typically particles form spatial arrangements after long aging times, for example they align along the soft  $\langle 001 \rangle$  elastic directions and in some cases form groups of many particles. HREM has been used to acquire images including the particle matrix interphase. The selected zone axis is [001]. The quantitative analysis to determine the positions of the intensity maxima and the subsequent evaluation of the lattice parameters, is made by using the software Darip. Two different directions with respect to the particle matrix interface (parallel and perpendicular) are considered for the evaluation. These measurements are compared to determinations made by means of quantitative evaluation based on calibrated CBED patterns taken from similar regions of the samples.

Work supported by CONACYT (Proy. 28952U) and COFAA-IPN.

#### Q4.11

**TEM STUDIES OF UNUSUAL MICROSTRUCTURES WITH INTERNAL LATTICE BENDING FORMED IN CRYSTALLISED AMORPHOUS FILMS.** Vladimir Yu. Kolosov, Lev M. Veretennikov, Ural State Economic Univ, Engineering Dept, Ekaterinburg, RUSSIA; Anders R. Tholen, Chalmers Univ of Technology, Dept of Experimental Physics, Goteborg, SWEDEN.

Amorphous films and thin layers have various areas of applications (e.g., in microelectronics and information storage) and their crystallisation (either undesirable or desirable) is of prime interest. Numerous bend contours are often inherent in TEM micrographs of crystallised areas. It was shown earlier that often they correspond to unusual microstructures with strong (up to 120° per micron) regular, dislocation independent internal bending of the crystal lattice planes [1]. TEM is the only suitable method for identification of such strong orientation gradients. In this paper we study (in part - in situ) the

influence of film thickness, composition and lattice orientation by means of bend-contour technique and high resolution imaging performed with a CM200FEG and a slowscan CCD camera. EDX, EELS and CBED are also used. For the crystallisation front moving to the thinner part of amorphous film evaporated with a strong thickness gradient (thickness range 100-15 nm) lattice bending, as well as irregularities in its geometry and grain boundary density, are strongly increasing, whereas the growth rate is going to and including zero. Crystal growth of hexagonal Se in Se-Te films with a gradient in relative concentration of elements was studied in the amorphous parts, enriched with Se. The magnitude of internal bending in Se crystals (for the growth rates in the range 0.5 - 1  $\mu\text{m/s}$ ) is built up upon the increase of Te content in amorphous film. HREM accompanied all the studies with most interesting results obtained for iron oxide films crystallising rhythmically with alternating annular zones of different contrast and imperfection. Most perfect and imperfect regions and the amorphous-crystalline interface at the moving crystallisation front are examined. I. Kolosov V. Yu., Proc. XII ICEM, Seattle, San Francisco Press, v. 1, 574 (1990). This work is partially supported by RSAS grant 1537 and RFBR grant 97-02-17784.

#### Q4.12

DIFFUSION ASSISTED DISLOCATION CLIMB IN INTERMETALLIC GAMMA-TiAl. Fritz Appel, GKSS Research Centre, Institute for Materials Research, Geesthacht, GERMANY.

Titanium aluminide alloys based on the intermetallic gamma TiAl phase have received increasing attention over the past decade due to their potential as high temperature structural materials. However, for technical applications the materials suffer from insufficient creep resistance at the intended service temperature of about 700°C. The paper reports an experimental study of diffusion controlled deformation mechanisms in two-phase titanium aluminides which apparently cause the degradation of the strength properties at elevated temperatures. Electron microscope in situ heating experiments and high resolution investigations were performed in order to characterize diffusion controlled dislocation climb. Climb velocities were analyzed in terms of diffusion coefficients and the critical vacancy supersaturation necessary for the operation of diffusion assisted dislocation sources. The experimental results will be discussed concerning the structural stability of gamma-base titanium aluminides and potential factors for improving the high temperature strength.

#### Q4.13

SPECIMEN CURRENT IMAGING OF DELAMINATION IN CERAMIC FILMS ON METAL SUBSTRATES IN THE SEM. Sрни Rangarajan, Alexander H. King, Dept. of Materials Science & Engineering, SUNY, Stony Brook, NY.

Plasma spraying of yttria-stabilized zirconia on stainless steel substrates generates rapidly solidified thin film discs called splats. Constraint due to adhesion at their interface generates sufficient stresses during cooling from the melting point to substrate temperature to generate extensive cracking. Stress relief by cracking is always accompanied by delamination of the thin films at the edges of cracked segments. It is shown here that images obtained in the SEM through amplification of the specimen current signal generate the right contrast for delineating regions of edge delamination in the cracked segments of a splat. Image analysis using this contrast provides a quantitative measure of the extent of delamination at the interface. Study of splats obtained on substrates at different temperatures reveals greater delamination at lower temperatures. Correlation also indicates complementary nature of stress relief by delamination and cracking. A detailed analysis including data from solidification and cooling and cracking statistics will give a measure of the adhesion strength at the interface. This technique is a quick method for measuring delamination of microscopic degree in thin films on conducting substrates. Acknowledgement: This work is supported by the National Science Foundation, MRSEC program, Grant No. DMR9632570.

#### Q4.14

APPLICATION OF TRANSMISSION ELECTRON MICROSCOPY FOR IN SITU STUDIES OF THE FORMATION OF INTERMETALLIC COMPOUNDS. Boris B. Bokhonov, Mikhail A. Korchagin, Institute of Solid State Chemistry, Siberian Branch of Academy of Sciences, Novosibirsk, RUSSIA.

In the present work, transmission electron microscopy was applied to the studies of structural and morphological characteristics during in situ interaction in metal systems. For this purpose, the pairs of interacting substances were chosen so that only one eutectic point was present in their phase diagrams Au-Si(Ge). Besides, the studies in the systems with unlimited solubility (Au-Ni, Cu-Au) and in the systems involving the formation of intermetallic compounds (Ni-Al, Au-Al, Ni-Si, Ni-Ge) were also performed. Electron microscopic studies were

carried out using the samples in which one of the interacting components was single crystal (or polycrystal) film or foil while the second component was present as a crystal particle of small size. The interaction between them was initiated with the help of a special heating unit or by the electron beam in the microscope with increased intensity. The application of this electron microscopic technique allowed us to obtain the data on the aggregate state of the reacting substances, the nature of transported particles and the ways of their transport; to reveal phase composition of the intermediate products and the sequence of stages through which the formation of the final product proceeds. Besides, the observations of the interaction allowed to make conclusions concerning the formation and the development of the defect structure at the interphase boundary between the interacting substances.

#### Q4.15

IN-SITU OBSERVATION OF MELTING AND SOLIDIFICATION. H. Saka, S. Arai, S. Tsukimoto, H. Ibuka, H. Matsuki, H. Miyai, K. Sasaki, Nagoya Univ, Dept of Quantum Engg and CIRSE, Nagoya, JAPAN; M. Konno, T. Kamino, Hitachi Science Systems. Ltd, Hitachinaka, JAPAN.

Melting and solidification in metallic and ceramic materials have been observed in situ inside transmission electron microscopes. The materials observed included pure Al, Al-Si, Al-Mg, Pb-Sn eutectic alloy, Al-Cu eutectic alloy and alumina. Structure and dynamical behavior of a solid-liquid interface during crystal growth were observed at near atomic resolution. EELS analysis was for the first time applied to liquid phases for the purpose of eventually making an elemental map in the liquid phase near a solid-liquid interface.

#### Q4.16

SITE OCCUPANCY DETERMINATION BY ALCHEMI OF Nb AND Cr ALLOYING ELEMENTS IN GAMMA TITANIUM ALUMINIDES. James Wittig, Lisha Wang, Tim Miller, Vanderbilt University, Nashville, TN; Ian Anderson, Oak Ridge National Laboratory, Oak Ridge, TN.

The site distributions of Nb and Cr alloying additions have been characterized in the L1<sub>0</sub>-ordered gamma-TiAl phase in ternary titanium aluminides subjected to a variety of heat treatments. This investigation is part of a wider study investigating the effects of transition metals on the structure and properties of ternary gamma-TiAl alloys. Site distributions have been characterized by atom location by channeling enhanced microanalysis (ALCHEMI). The processing of the alloys include conventional heat treatments, such as furnace cooling from the solutionizing temperature in the gamma single-phase field and water quenching from the gamma+alpha two-phase field, as well as rapid solidification from the liquid state by electromagnetic levitation and splat quenching. Preliminary ALCHEMI studies of the conventionally heat-treated alloys yield results generally consistent with those in the published literature. Nb alloying additions are found to partition exclusively to the 'Ti' sublattice, while Cr alloying additions exhibit an 'Al' sublattice preference, but with a wide range in the site-distribution, from 52% to 91% 'Al'-site occupancy, depending on alloy stoichiometry and thermal history. However, preliminary studies indicate that a higher degree of disorder can be achieved with rapid solidification. Significant partitioning of the Nb has been measured in the splat quenched alloys, with up to 12% occupying the 'Al' sublattice. The effects of these microchemical changes on the structure and mechanical properties of the alloys are being investigated.

#### Q4.17

ELECTRON CHANNELING X-RAY MICROANALYSIS FOR CATION CONFIGURATION IN IRRADIATED MAGNESIUM ALUMINATE SPINEL. Syo Matsumura, Takeshi Soeda, Chiken Kinoshita, Kyushu Univ, Dept of Applied Quantum Physics and Nuclear Engineering, Fukuoka, JAPAN; Nester Zaluzec, Materials Science Division, Argonne National Laboratory, Argonne, IL.

Magnesium aluminate spinel compounds (MgO/Al<sub>2</sub>O<sub>3</sub>) are drawing much interest to their potentials in electric insulators for future fusion reactors, because of their excellent radiation resistance. In the ideal structure of MgO/Al<sub>2</sub>O<sub>3</sub>, Mg<sup>2+</sup> and Al<sup>3+</sup> ions occupy 1/8 of the tetrahedral sites (T-sites) and 1/2 of the octahedral ones (O-sites), respectively, of the fcc lattice of O<sup>2-</sup> ions. The reliable stability in radiation fields is believed to come from the considerable amount of unoccupied sites, which would accommodate displaced ions and would suppress nucleation of defect clusters under irradiation. The present study is intended to validate electron channeling enhanced x-ray microanalysis as a tool to measure radiation-induced cation displacements in MgO/Al<sub>2</sub>O<sub>3</sub>. In the experiment, TEM specimens of MgO/Al<sub>2</sub>O<sub>3</sub> annealed at 1470 K for 48 hours were irradiated at 870 K to a dose of about 2 dpa with 1 MeV Ne<sup>+</sup> ions or 900 keV electrons. X-ray emission from the specimens was measured as a function of



electron beam rocking between  $-16,0,0$  and  $16,0,0$  Bragg positions at an accelerating voltage of 120 or 200 kV. In unirradiated or undamaged areas, the rocking curves of characteristic x-ray emission show strong dependence on the diffraction condition of incident electrons. They suggest that about 80% of  $Mg^{2+}$  ions and about 90% of  $Al^{3+}$  ions are located on T-sites and O-sites, respectively, while the rests are on the opposite sublattices. The characteristic x-ray emission becomes less dependent on the diffraction condition for damaged regions, owing to disordering. In regions irradiated to 2 dpa with 900 keV electrons,  $Mg^{2+}$  ions on T-sites and  $Al^{3+}$  on O-sites decrease to about 54% and about 77%, respectively. Almost similar degree of disordering is found in a pre-peak damaged region in a cross-sectional specimen irradiated with 1 MeV  $Ne^+$  ions, where no extended defects are recognized in electron micrographs. Thus, the electron channeling enhanced x-ray microanalysis possesses significant sensitivity to detect cation displacements in spinel compounds. A part of the present work was carried out using a CM200 at Oak Ridge National Laboratory through the courtesy of Dr. Ian Anderson and Dr. Jim Bentley.

#### Q4.18

ORDERING IN TERNARY B2 ALLOYS. S. Amancherla, R. Banerjee, Hamish L. Fraser, Ohio State University, Dept. of Materials Science and Engineering, Columbus, OH; S. Banerjee, Materials Group, Bhabha Atomic Research Center, Bombay, INDIA.

The properties of ordered intermetallic materials, especially their mechanical properties, are often strongly dependent on the type and degree of ordering in such materials. Therefore, a better understanding of the complex ordering schemes in these materials will assist in understanding as well as tailoring their properties. One of the most commonly observed ordering schemes in bcc based intermetallic alloys is the B2 structure which divides the bcc lattice into two primitive cubic sublattices. In binary B2 alloys, the long range order (LRO) can be described in terms of a single LRO parameter which makes the description of the ordering state relatively simple. However, in ternary intermetallic alloys, two independent LRO parameters are required in order to describe the complex ordering schemes which can develop. An elegant graphical description of the ordering in ternary B2 alloys is the Ordering Tie Line (OTL) which allows a simple visualization of the ordering schemes while rigorously encompassing the information of the two LRO parameters. This paper will focus on the ordering schemes in ternary B2 alloys based on the Nb-Ti-Al system as well as Fe-Al and Ni-Al systems with ternary additions. Atom location by channeling enhanced microanalysis (ALCHEMI) has been used to determine the relative site preferences of the various elements (the slope of the OTL) which is one of the order parameters. Subsequently, the length of the OTL has been calculated based on the dynamical theory of electron diffraction using a 17-beam approximation. In addition, the OTLs have been calculated using a model based on an reaction rate approach to predicting equilibrium configurations in ternary B2 alloys. The model is based on the classical Bragg-Williams theory of order-disorder transformations and uses a nearest-neighbor approximation. A comparison of the calculated and experimentally determined results will be presented emphasizing on the power of the OTL representation.

#### Q4.19

IN SITU STUDIES OF STABILIZATION OF ZIRCONIA BY MN OR N SUBSTITUTION. Renu Sharma, Center for Solid State Science Arizona State University, Tempe AZ; Dirk Naedele and Eberhard Schweda, Anorganische Chemie, Universitat Tübingen, Tübingen, GERMANY.

Zirconia has been one of the most important ceramic materials for decades due to its many useful mechanical and electrical properties. Among them most important is the high oxygen storage capacity and high ionic conductivity. But the room temperature form of pure zirconia (monoclinic phase) undergoes the first reversible transformation to a tetragonal form at  $1100^{\circ}C$  and then to a cubic form at higher temperatures. The 4% volume change due to the monoclinic to the tetragonal phase transformation results in formation of cracks, thus restricting the use of material to a much lower temperatures. It has been established that the addition of oxides, e.g.  $MgO$ ,  $CaO$  and  $Y_2O_3$ , allows the cubic form of zirconia to be stable from room temperature to melting point. We have found that the cubic zirconia can be stabilized by adding either Mn or by heating amorphous  $Zr(OH)_2$  in  $NH_3$  at elevated temperatures ( $1100^{\circ}C$ ). We have used time and temperature resolved x-ray-diffraction, electron diffraction, high resolution electron microscopy and electron energy loss microscopy to follow the reaction processes involved. The study of nucleation and growth process of Mn-doped zirconia has revealed the crystal size to be an important stabilization factor. We have also found that the N substitution for O in the lattice is another way for not only creating O vacancies but also stabilizing cubic for zirconia. The chemical and structural changes during the nucleation and growth process will be discussed in detail.

SESSION Q5: POSTER SESSION:  
SPECIMEN PREPARATION AND  
MICROELECTRONIC MATERIALS  
Chairs: Dean J. Miller, Ray D. Twesten and Yimei Zhu  
Wednesday Evening, December 1, 1999  
8:00 P.M.  
Exhibition Hall D (H)

#### Q5.1

FOCUSED ION BEAM (FIB) SYSTEM: MORE THAN JUST A FANCY IBT. Steven Kim and Vinayak P. Dravid, Northwestern Univ., Dept of MS&E, Evanston, IL.

With shrinking dimensions of devices and associated phenomena, it has become necessary to manipulate and analyze materials structures at nanometer length-scale, with site-specificity of similar order. Focused ion beam (FIB) systems, which are now readily and commercially available, greatly facilitate such tasks. During the 1990's FIB machines have become far more sophisticated than their past counterparts, with extensive computer control, compatibility with SEM/TEM stages, fine probe forming capability ( $< 10\text{-}20\text{ nm}$ ) coupled with adequate beam current for sputtering and deposition. In TEM community, however, FIB are often associated with thin foil specimen preparation, especially for difficult materials systems (e.g. composites, metal-semiconductor systems etc.) where traditional ion beam thinners (IBTs) suffer in many ways. However, the site-specificity of FIB and its ability to sputter/deposit a wide range of materials have opened several niche and unusual applications. This presentation will cover not only the 'traditional' role of FIB in making electron transparent TEM foils of 'difficult' materials but highlight some emerging and niche applications in nano/micromanipulation. The great ability of modern FIB in making site-specific thin sectioning will be demonstrated for ceramic-matrix-composites (CMCs) where conventional specimen preparation often leads to differential thinning, cracking and drop-outs of weakly bonded fibers. In thin films, FIB site-specificity is extremely useful in monitoring growth processes by creating thin 'plan-view' sections at various depths in thin films. The emergence and complex propagation of threading dislocations in lateral epitaxial growth (LEO) of GaN films will be demonstrated. Finally, novel and unusual application of FIB in creating trenches for microfluid dynamics, site-specific electrode deposition, AFM tip synthesis etc. will be presented.

#### Q5.2

TEM SAMPLE PREPARATION USING FIB/SEM DUALBEAM TECHNIQUE. Sean Da, Y.C. Wang, FEI Company, Hillsboro, OR.

Nowadays, semiconductor structure has been constantly shrinking to a much smaller feature size ( $< 0.25\mu m$ ). The use of FIB (Focus Ion Beam)/SEM (Scanning Electron Microscope) combined (Dualbeam) system will provide the site-specific capability for the TEM sample preparation. Because of the destructive properties of the ion beam, the FIB prepared TEM sample will be limited in finding a sub-micron feature. The slicing and viewing capabilities of the Dualbeam FIB system will precisely locate the buried feature without the unnecessary ion damage. While FIB sectioning the sample, the E-beam can be used to monitor the whole process. Different gas environment can be introduced to the ion chamber for implementing the selective etching and pattern editing. For a sub-micron feature on the surface, the FIB system offers a metal deposition ability to protect the interested area during FIB sectioning. The scripting automation coupled with the manual trimming of the digital FIB system opens an area for unattended TEM sample preparation. Some determined parameters to avoid the ion beam damage and different FIB TEM sample preparation technique will be discussed in the presentation.

#### Q5.3

AUTOMATED CLEAVING AND DUALBEAM TECHNIQUES FOR SITE SPECIFIC SAMPLE PREPARATION AND HIGH RESOLUTION SEM IMAGING. Janet Teshima, FEI Company, Hillsboro, OR; Efrat M. Raz, SELA, Santa Clara, CA; Fred Clark, Texas Instruments, Dallas, Texas Mike Dennis, FEI Company, Hillsboro, OR.

The semiconductor industry is continuously driven to improve performance and time to market while controlling manufacturing costs. The sources of many defects are identified by in-line inspection tools inside the wafer fab, however the most insidious subsurface and electrical defects must be characterized out of the fab in the lab environment. With current semiconductor technologies typically less than  $25\text{-micron}$ , it is becoming increasingly difficult to achieve sub-micron accuracy, on a consistent basis, using mechanical polishing or manual cleaving techniques. In this case study, we have used the automated microcleaving technique to prepare the sample for final FIB (Focused Ion Beam) polish and high resolution SEM (Scanning

Electron Microscopy) imaging in a dual beam (FIB/SEM) workstation. The MC200 microcleaving system accurately and automatically cleaves close to the area of interest, positioning the target less than one-micron from the edge, in less than 10 minutes. The sample can then be milled and imaged with a dual beam, which takes typically 3-5 minutes of milling. By combining these technologies, the sample can be viewed at an orientation normal to the SEM column. It allows obtaining highest resolution SEM images, best X-ray collection, and most accurate metrology on cross-section. The quality of the sample is improved and the overall sample preparation time is reduced dramatically.

#### Q5.4

##### ENVIRONMENTAL SCANNING ELECTRON MICROSCOPY AS A TOOL FOR MICROCRACK STUDIES IN CONCRETE.

Jan Bisschop, Jan van Mier, Delft Univ of Technology, Dept of Civil Engineering and Geosciences, Delft, THE NETHERLANDS.

During the hardening of concrete the cement fraction shrinks due to loss of water from pores caused by drying and hydration processes. Microcracking due to this shrinkage may influence the durability or mechanical behavior of the concrete. To quantify the severity of shrinkage microcracking a consistent and reliable microcrack detection technique is needed. The destructive techniques (fluorescence microscopy and conventional SEM) that are used to quantify microcracks in concrete have one major drawback: the concrete is dried during sample preparation. This drying causes opening and formation of new microcracks on the sample surface. Therefore reliable quantification of 'real' microcracks is not possible. Environmental Scanning Electron Microscopy does not involve any drying of the concrete samples, and therefore is a very promising tool for the quantification of shrinkage microcracking. In ESEM concrete samples can be examined at relative humidities of 90-100%, thus the 'internal' microcrack pattern is recorded only, without any risk of introducing additional cracks. Experiments are carried out, in which concrete specimens are dried outside the chamber. At different intervals during drying ESEM-samples are prepared and a map of the temporary microcrack pattern is produced using ESEM. In addition, dynamic experiments are performed in the ESEM to follow the development of the surface cracking pattern as a function of relative humidity and drying time. In this contribution the experimental procedures will be described. Emphasis lies on the sample preparation technique and on the control of the relative humidity immediately above the sample surface. The results of the experiments are presented in detail in symposium GG.

#### Q5.5

MICROCHARACTERIZATION OF COMPLEX SPECIMENS OF ENVIRONMENTAL INTEREST CONTAINING TIRE DUST: DEVELOPMENT OF SPECIMEN PREPARATION METHODS AND ANALYTICAL PROCEDURES. Marina Camatini, Gaia Corbetta, Giovanni F. Crosta, DiSAT, Università di Milano Bicocca, Milano, ITALY; Giampaolo Giuliani, Pirelli Pneumatici, Milano, ITALY; Tigran Dolukhanyan, Changmo Sung, Dept. of Chemical Engineering, University of Massachusetts-Lowell, Lowell, MA.

Particulates produced by automotive traffic contained complicated species such as combustion products and debris from the wear of brakes, tires and the road surface. These particles had an impact on human health and environmental compartments and information on the identification of particles will be required in order to assess their impact. Besides the elemental analysis of a bulk specimen by the conventional wet chemistry, the size, shape and chemistry of the particles must be carefully examined on a microscale since each constituent will form variety of morphological, physical and chemical phases. The tire dust samples were most challenging problems since the original rubber consisted of composite materials, known to contain styrene-butadiene copolymer, fillers, Zn and S compounds. The experimental results reported herewith were obtained from both homogeneous (tire dust alone) and heterogeneous specimens (mixtures of tire dust with other mineral and organic particles) in order to understand characteristics of each element. The microcharacterization of tire dust appeared to be feasible to solve and prevent environmental issues, provided SEM and TEM analyses were properly combined with EDXS and CBED techniques along with sophisticated sample preparation methods.

#### Q5.6

##### INCOHERENT HIGH RESOLUTION Z-CONTRAST IMAGING OF SILICON AND GALLIUM ARSENIDE USING HAADF-STEM.

Yasutoshi Kotaka, Yoshio Kikuchi, FUJITSU LABORATORIES LTD., Kanagawa, JAPAN; Takashi Yamazaki, Department of Physics, Science University of Tokyo, Tokyo, JAPAN; Kazuto Watanabe, Tokyo Metropolitan College of Technology, Tokyo, JAPAN.

The using of a high angle annular dark field (HAADF) technique in a dedicated scanning transmission electron microscope (STEM) is

performed to provide incoherent images of crystalline materials with strong compositional sensitivity dependent on atomic number (Z-contrast image). Furthermore, a high spatial resolution image close to sub-angstrom obtained by HAADF technique is comparable to the conventional coherent imaging (HRTEM). But it is difficult to obtain a clear atomic structure image of HAADF using a hybrid TEM-STEM system because the optics of a hybrid TEM-STEM is different from that of a dedicated STEM. HAADF images are obtained JEOL JEM-2010F with thermal-schottky field emission gun in probe-forming mode at 200keV. We performed an experiment using Si for observation of high resolution image and GaAs for Z-contrast image identifying each atoms in the [110] zone axis direction. The conditions of electron optics of HAADF-STEM mode was optimized to change sample thickness, detector inner and outer angle, convergent semi-angle and defocus. As a result, high resolution HAADF images of Si [110] are showing the dumbbells structure corresponding to [004] spacing 0.136nm. The intensity profiles of Ga and As along 001 direction are showing different intensities between each atoms. The experimental image was analyzed and was compared with the calculated atomic position and intensities depending on atomic number obtained from the Bethe's eigen-value method for inclined illumination. This calculation was modified to simulate HAADF-STEM based on L.J. Allen and C.J. Rossouw's method for CBED. A. Weickenmeier and H. Kohl's absorptive scattering factor for high angle scattering was used in this calculation. The experimental result showed a good agreement with the simulation result.

#### Q5.7

THE ATOMIC STRUCTURE OF MOSAIC GRAIN BOUNDARY DISLOCATIONS IN GaN EPITAXIAL LAYERS. Valerie Potin, Gerard Nouet, Pierre Ruterana, Laboratoire d'Etudes et de Recherches sur les Matériaux, UPRESA CNRS 6004, ISMRA, Caen, FRANCE; Robert C. Pond, Dept of Materials Science and Engineering, University of Liverpool, Liverpool, ENGLAND.

In GaN epitaxial layers, due to the mosaic growth mode, a large density of threading dislocations are present bounding slightly misorientated grains ( $T < 3^\circ$ ). Using high resolution electron microscopy, anisotropic elasticity calculations and image simulations, typical contrast was identified for these defects. The atomic structure of the edge threading dislocations was found to exhibit 5/7 and 8 cycles. These two configurations were observed at a similar frequency for isolated dislocations and low angle grain boundaries. Besides these low-angle grain boundaries, high-angle grain boundaries can be present as well. Adjacent crystals are rotated around (0001) and the interfacial structures can be described in terms of coincidence site lattices (CSL): S=7 ( $T=21.79^\circ$ ), S=19 ( $T=13.17^\circ$ ), S=31 ( $T=17.89^\circ$ ). CSL model is deduced by considering two identical interpenetrating lattices. If one lattice is rotated through a common lattice point, for certain angles, site lattices come into coincidence, forming the so-called coincidence lattice. Sigma corresponds to the ratio of the volume of the CSL unit cell and the primitive lattice. Here, we present an analysis of the S=7 boundary using circuit mapping in order to define the Burgers vectors of the dislocations. In the analysed micrographs, the boundary is symmetric in certain areas in which case the boundary plane was found to be (21-30) and the periodic structure is comprised of an array of only one dislocation type, although the cores of these defects possess more than one atomic configuration. The interface sometimes exhibits asymmetric boundary planes with (3-85)1 / (10-10)2 and the periodic structure can be described in terms of four dislocation's cores. In these boundaries, the previous models with 5/7 and 8 atom cycles are present and the 4 atom ring configuration was identified as well. Interface steps have been identified some of which have a defect character, in such cases the defect may correspond to a modification of the core structure of one or more interface dislocation.

#### Q5.8

INTERFACE STRUCTURE AND Zn DIFFUSION IN CdTe/ZnTe/Si SYSTEM GROWN BY MBE. S.-C.Y. Tsen, David J. Smith, P.A. Crozier, Arizona State Univ, Center for Solid State Science, Tempe, AZ; S. Rujirawat, S. Sivananthan, Univ. of Illinois at Chicago, Microphysics Laboratory, Department of Physics, Chicago, IL.

Two sets of CdTe/ZnTe/Si samples were grown by MBE on Si (211) and (111) substrates for use as lattice-matched substrates for HgCdTe growth. An As precursor was used in some cases before growing ZnTe. In order to understand the interface structure and the Zn diffusion due to annealing, high resolution bright field images, dark field images and energy-dispersive X-ray spectroscopy (EDS) techniques were used. Fourier filtered images revealed the detail of the atomic arrangements and the defects at the interface. The local lattice parameters such as (111) spacings were measured to estimate the Zn concentration at different distances from the interface using Vegard's law, and the results were compared with EDS measurements. Sharp interfaces with misfit dislocations, and broader interfaces with interfacial layers, misfit dislocations and stacking faults were observed. Possible

interfacial phases will be discussed based on analysis of dark field images, local lattice parameter measurements and the EDS results.

#### Q5.9

STEM/EELS CHARACTERIZATION OF SILICON OXYNITRIDES WITH AN ATOMIC-SCALE RESOLUTION. Sanjit Singh Dang, Teya T. Topuria\*, Nigel D. Browning\* and Christos G. Takoudis, Advanced Materials Research Laboratory, Department of Chemical Engineering, University of Illinois at Chicago, Chicago, IL; \*Department of Physics, University of Illinois at Chicago, Chicago, IL.

The semiconductor industry has experienced a continuous evolution in the device technology for almost the last three decades. The trend of device scaling requires shrinking both the horizontal features (e.g., channel length and width) as well as the vertical features (e.g., junction depth and dielectric thickness). As a result, the reliability of ultra-thin oxide (< 5nm thick) becomes critical for performance of gate and tunnel dielectrics in metal-oxide-semiconductor field effect transistor (MOSFET) and electrically erasable programmable read-only memory (EEPROM) structures, respectively. Boron (used to dope polySi to form p+ gate) can penetrate through thin oxides into the channel region, leading to degradation of the electrical properties. With the incorporation of nitrogen into the oxide (resulting in what is called the 'silicon oxynitride'), improvements in boron penetration resistance, MOSFET performance and reliability, tunnel dielectric endurance, dielectric charge to breakdown, and resistance to plasma damage have been reported. Since the performance of the oxynitride film depends upon its chemical composition and state, a prior thorough understanding of these properties is essential. To achieve this, atomic-scale characterization of the nitrogen distribution in these films with angstrom accuracy is required. A Scanning Transmission Electron Microscope (STEM), equipped with Electron Energy Loss Spectroscopy (EELS), is used to explore the bonding structure in the silicon oxynitride film, especially at the interface, with an atomic-scale resolution (<2Å). This study may show light on the interfacial physico-chemical properties of oxynitrides, ignored by the conventional techniques (such as x-ray photoelectron spectroscopy (XPS)) due to a lower resolution. Such results may be extremely helpful towards establishing knowledge-based fabrication methodologies of future ultra-thin dielectrics.

#### Q5.10

TANTALUM AS DIFFUSION BARRIER LAYER BETWEEN COPPER AND Si: FAILURE MECHANISM AND EFFECT OF OXYGEN. Kai-Min Yin, Fu-Rong Chen, Ji-Jung Kai, Dept of Engineering and System Science, National Tsing Hua University, Hsinchu, Taiwan, ROC; Peijun Ding, Barry Chin, Hong Zhang, Fusen Chen, Metal Deposition Products Group, Applied Materials, Santa Clara, CA.

High-resolution TEM and electron energy loss spectrometer (EELS) were used to investigate the thermal stability of Ta barrier layer and the mechanism for Cu penetrating through barrier layer at various high temperatures anneal. The thin films Ta(25 nm)/Cu(150nm) were deposited onto (001) silicon substrate using ionized metal plasma technique (IMP) process under ultra-high vacuum condition ( $1 \times 10^{-8}$  torr). Transmission electron microscopy (TEM) demonstrates as deposited Ta film is a nano-crystalline beta phase. Samples annealed at 350, 400, 500, 550 and 600°C in Ar atmosphere. For temperature lower than 600°C, oxygen diffuses through the grain boundaries of Cu films and reacts with Ta film to form amorphous TaO<sub>x</sub> film between the interface of Cu and Ta. At 600°C, Ta and Si first reacted into Ta<sub>5</sub>Si<sub>3</sub>, then the Cu diffusion transformed the structure of Ta<sub>5</sub>Si<sub>3</sub> to TaSi<sub>2</sub> and both η' and η Cu<sub>3</sub>Si phases would form in Si substrate. At 600°C, oxygen from outside atmosphere could also diffuse through TaSi<sub>2</sub> and oxides part of Cu<sub>3</sub>Si to form silicon dioxide. This report proposes that the coexistence of η' and η'' of Cu<sub>3</sub>Si phases after 600°C annealing may be due to the oxidation process can slow phase transformation from η' to η''. This result is in contrast to some previous observations only one η' phase exists in high temperature.

#### Q5.11

TEM AND HREM STUDY OF BLISTERING IN HYDROGEN IRRADIATED SILICON LAYERS ANNEALED AT HIGH PRESSURE. V.P. Popov, A.K. Gutakovskiy, A.I. Antonova, Institute of Semiconductor Physics, Novosibirsk, Russia; A.Romano-Rodriguez, A.Bachroui, University of Barcelona, Department of Electronics, Barcelona, SPAIN; A. Misiuk, Institute of Electron Technology, Warsaw, POLAND; Ja. Back-Misiuk, Institute of Physics, Warsaw, POLAND.

Hydrogen implanted silicon layers have been successfully used for Silicon-On-Insulator (SOI) creation. Fundamental phenomenon of blistering at ion irradiation is in the base of this method. However ion implantation has a major shortcoming connected with the need of removing residual defects interacting with each other and hydrogen

atoms. Only simple defects are introduced during light hydrogen ion irradiation: vacancies (V) and self interstitials (I). Their concentrations are only slightly larger than implanted H atoms. These defects can annihilate, cluster, and lead to the formation of well-known platelets with {111} or {100} habitus planes during irradiation. It was supposed that VH<sub>2</sub> and IH<sub>2</sub> defects move fast to platelets, and annihilate at their walls leading to an increase in H<sub>2</sub> gas content inside the extended defects and their growth at annealing with constant gas overpressure up to microcrack creation. The alternative mechanism invokes buildup of lateral stresses introduced during ion bombardment. Opposite, it was shown by us, that blistering and exfoliation are enhanced in silicon highly doped with boron in substitutional position without stresses on the defects following boron implantation. The influence of supplementary stresses during annealing at 500 - 1130°C caused by high external hydrostatic pressure up to 1.5 GPa on the extended defect formation was investigated in hydrogen implanted Si wafers by plan view and cross section TEM and HREM. Suppression of blistering and exfoliation, and clear microscopic picture of defects and their evaluation was obtained.

#### Q5.12

RELATIONSHIP BETWEEN MICROSTRUCTURE AND LUMINESCENT PROPERTIES OF EPITAXIALLY GROWN Y<sub>2</sub>O<sub>3</sub>:Eu THIN FILMS ON LaAlO<sub>3</sub> SUBSTRATES. H.-J. Gao, A. Kadavanichi, X.D. Fan, S.J. Pennycook, Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN; D. Kumar, K.G. Cho, P.H. Holloway, R.K. Singh, Department of Materials Science and Engineering, University of Florida, Gainesville, FL.

Yttrium oxide (Y<sub>2</sub>O<sub>3</sub>) thin films have attracted considerable interest for various applications in ultra-large scale integration (ULSI) gate insulators, ULSI capacitors, and, doped with europium (Eu), for electroluminescence devices. Transmission electron microscopy (TEM), x-ray, and Z-contrast scanning transmission electron microscopy (Z-STEM) were employed to relate the microstructure, interface structure, and cathodoluminescent (CL) properties of the laser ablation deposited films. Due to the 0.8% lattice mismatch, epitaxial growth of Y<sub>2</sub>O<sub>3</sub>:Eu thin films was obtained on LaAlO<sub>3</sub> (001), with the orientation relationship [110]Y<sub>2</sub>O<sub>3</sub>//[100]LaAlO<sub>3</sub> and [-110]Y<sub>2</sub>O<sub>3</sub>//[010]LaAlO<sub>3</sub>. STEM imaging of the films shows the substrate always terminates with the Al sublattice. No Eu precipitates were observed. The Y<sub>2</sub>O<sub>3</sub>:Eu thin films, although good single crystals, contain a large density of small pores, which strongly affect their luminescent properties. It is known that surfaces act as non-radiative recombination sites for luminescence, creating a "dead layer" with thickness of the order of the carrier diffusion length. The pores create significant internal surface area, so that luminescent efficiency is directly correlated with pore density. Using the nanometer-scale probe in our Z-contrast STEM, the CL properties can be mapped at nanometer resolution. CL images of the films provide direct observations of the dead layer. CL spectroscopy reveals the role of other structural defects.

#### SESSION Q6: PARTIALLY ORDERED AND NANOPHASE MATERIALS

Chairs: Charles W. Allen and David J. Smith  
Thursday Morning, December 2, 1999  
Salon A/B (M)

#### 8:30 AM Q6.1

IMAGING HETEROPHASE MOLECULAR MATERIALS IN THE ENVIRONMENTAL SCANNING ELECTRON MICROSCOPE. Athene M. Donald, Bradley L. Thiel, Debbie J. Stokes, Ian C. Bache, Robert G. Mathews, Cavendish Laboratory, University of Cambridge, UK.

Environmental Scanning Electron Microscopy (ESEM) obviates the need for conductive coatings to be applied to insulators due to the presence of a gas in the chamber. It also permits fluids to be imaged in their native state. These advances have as yet been little appreciated. In the absence of a coating, the secondary electron image in heterophase materials is due to inherent variations in secondary electron emission. For both polymers and molecular fluids there can be quite substantial variations in the emissivity between species, giving rise to significant contrast. This paper will study the structure in two different classes of systems: fully fluid oil-water emulsions and phase separation in polymer mixtures, where there is no need for the polymers to be stained.

#### 8:45 AM \*Q6.2

THE CHEMICAL WIDTH OF POLYMER INTERFACES. M. Libera, Stevens Institute of Technology, Hoboken, NJ.

The width of polymer interfaces in blends and composites is

determined by a balance between entropic and enthalpic forces which define the number and nature of entanglements across an interface. The widths characteristic of such interfaces have traditionally been studied using X-ray and neutron scattering, but these techniques typically require one-dimensional planar interfaces. Because of their high-spatial resolution, methods based on electron scattering are better suited for studies of interfacial structure in the more technologically-relevant situation where one phase is finely dispersed in another. This presentation describes the application of spatially-resolved electron energy-loss spectroscopy to the measurement of interfacial width in homopolymer blends of poly(2-vinyl pyridine) [PVP] dispersed in poly(styrene) [PS]. The measurement determines the fraction of nitrogen, characteristic of the PVP phase, as a function of position across an unstained PS-PVP interface. The effects of probe broadening and interfacial curvature are estimated and deconvoluted from the measured data to give an upper bound to the chemical width of 3.5 nm in good agreement with independent measurements by neutron scattering. Dose-resolved studies show that mass loss during the eels measurements is insignificant. In addition, quantitative analysis using the background-subtracted C and N K-edges in PVP finds a carbon/nitrogen ratio of  $7.05 \pm 0.20$ . The stoichiometric value is 7.0. The presentation concludes with brief mention of parallel studies of interphases in fiber-reinforced epoxies based on spatially-resolved energy-loss measurements of local aromaticity .

#### 9:15 AM \*Q6.3

TRANSMISSION ELECTRON MICROSCOPY IN BIOMIMETICS. Mehmet Sarikaya, Materials Science and Engineering, University of Washington, Seattle, WA.

Biomimetics is materials science and engineering through biology. Biological hard tissues, such as bone, dental tissues (dentin and enamel), mollusc shell structures, protozoan and echinoderm skeletal units, sponge spicules, and bacterial and algal ultrafine particles, have unrepresented physical (mechanical, magnetic, optical) properties, developed over 3.5 billion years of evolution. These properties result from highly ordered nano- and micro-structures of biological composites that self-assemble, often, into hierarchical architectures at ambient conditions under the genetic control of organisms. Mimicking biological design and synthesizing biologically-inspired novel, future materials and engineering systems require understanding of structure-function correlation in biomaterials and deciphering mechanisms of bio-materialization. Transmission electron microscopy techniques are proving to be invaluable tools in studying structures, crystallography, morphogenesis, and physico-chemical properties of biological hard tissues at the highest spatial resolution levels possible. Since biomaterials have hybrid structures, i.e., composites of biomacromolecules (proteins, polysaccharides, and lipids) and biominerals (such as  $\text{CaCO}_3$ , CdS,  $\text{Fe}_3\text{O}_4$ , and  $\text{SiO}_2$ ), both the electron-transparent sample preparation and TEM observation require prevention of radiation damage. We have developed several sample preparation protocols and studied a wide variety of biological materials relevant to materials science by TEM imaging (via diffraction and phase contrast), nano-diffraction, and (ELS) spectroscopy techniques. The biostructures to be discussed include nanolayered composites and their local dielectric functions in mollusc shells (piezoelectric), ordering of magnetite particles in magnetotactic bacteria (magnetic), coherent ceramic precipitates in sea-urchin spines (mechanical), the nature of the amorphous silica in sponge spicules (optical), and ultrafine hydroxyapatite crystallites in dental tissues of human and transgenic mice (protein effects). A broad view of these studies will be presented with a focus on structural lessons from biology towards materials science applications.

#### 10:15 AM Q6.4

MEASURING THE PHYSICAL PROPERTIES OF INDIVIDUAL NANOSTRUCTURES BY IN-SITU TEM. Z.L. Wang, School of Material Science and Engineering, Georgia Institute of Technology, Atlanta, GA.

Nanomaterials have distinctly different properties from bulks because of their unique crystal and electronic structures. Characterizing the physical properties of individual nanocrystals/nanostructures, however, is rather challenging because of the difficulty in manipulating the objects of sizes from nanometer to micrometer. New methodologies and approaches must be developed. In-situ transmission electron microscopy has been developed as a new technique for measuring the properties of individual nanostructures. Using a customer-built specimen holder, the quantum conductance of a carbon nanotube has been observed in-situ in TEM, confirming the ballistic conductance and no-heat dissipation across a defect-free nanotube [1]. In-situ measurements on the mechanical properties of carbon nanotubes has been carried out in-situ in TEM using the dynamic resonance phenomenon. An individual carbon nanotube was set to resonance by applying an alternating voltage across the electrodes. Resonance occurred once the applied frequency reached the mechanical resonance frequency, a quantity determined by the bending

modulus of the tube, its density, diameter and length. This gives a precise technique for measuring the bending modulus of a single carbon nanotube as a function of its diameter. The bending modulus for tubes smaller than 10 nm in diameter can be as high as 1 TPa, while those with sizes larger than 20 nm can be as low as 0.2 TPa. A nanotube has been demonstrated as a nanobalance for measuring the mass of a single nanoparticle in the range of femtograms, equivalent to the mass of a single virus [2]. [1] S. Frank, P. Poncharal, Z.L. Wang, and W.A. de Heer, Science, 280 (1998) 1744. [2] P. Poncharal, Z.L. Wang, D. Ugarte and W.A. de Heer, Science, 283 (1999) 1513. [3] Research supported by NSF DMR-9971412 and DMR-9733160.

#### 10:30 AM Q6.5

ELECTRON MICROSCOPY OF SINGLE MOLECULES. David E. Luzzi, Brian W. Smith, Univ of Pennsylvania, Dept of Materials Science, Philadelphia, PA.

The characterization of organic materials has always been a special challenge. In many cases, the molecular structure can be solved only after painstaking growth of single crystals. The weak scattering of electrons inherent to these materials requires that they be essentially suspended in vacuum in order to provide a sufficient signal above background in the electron microscope. We have recently identified a new class of materials, nanoscopic hybrid materials composed of Fullerenes, including  $\text{C}_{60}$ , encapsulated within single wall carbon nanotubes (SWNTs) of commensurate diameter. One of the intriguing properties of these materials is the stabilizing effect of the SWNT on individual Fullerene molecules.  $\text{C}_{60}$  molecules are routinely imaged and analyzed either lying within SWNTs or resident on the exterior surface. The SWNTs act as one-dimensional substrates that allow the imaging and spectroscopy of molecules stably suspended in the vacuum of the microscope. In this paper, these nanoscopic hybrid materials will be introduced. The synthesis, specimen preparation and electron microscopy will be described and the application of this approach to the analysis of other molecular materials will be presented.

#### 10:45 AM Q6.6

NANOCRYSTAL THICKNESS INFORMATION FROM Z-STEM: 3-D IMAGING IN ONE SHOT. Andreas V. Kadavanich, Tadd Kippeny, Meg M. Erwin, Sandra J. Rosenthal, Vanderbilt University, Dept. of Chemistry, Nashville, TN; Stephen J. Pennycook, Oak Ridge National Laboratory, Solid State Division, Oak Ridge, TN.

We have applied Atomic Number Contrast Scanning Transmission Electron Microscopy (Z-Contrast STEM) [Nellist, 1998 #964] towards the study of colloidal CdSe semiconductor nanocrystals embedded in MEH-PPV polymer films. In the thickness regime studied, the image intensity is a monotonic function of thickness. Hence an atomic column-resolved image provides information both on the lateral shape of the nanocrystal, as well as the relative thickness of the individual columns. Therefore, we obtain information on all three dimensions of the nanocrystal directly from the Z-Contrast image without the need for extensive image simulation. We show that the Z-Contrast image of a single CdSe nanocrystal is consistent with the predicted 3-D model derived from considering HRTEM images of several nanocrystals in different orientations. We further discuss the possibility of measuring absolute thicknesses of atomic columns if the crystal structure is known.

#### 11:00 AM Q6.7

ELECTRONIC STRUCTURE AND BONDING AT THE Ni-SiO<sub>2</sub> INTERFACE AS REVEALED BY ELECTRON ENERGY-LOSS SPECTROMETRY. Seth T. Taylor and Ron Gronsky, Univ of California, Dept of Materials Science and Mineral Engineering, Berkeley, CA.

Electron energy-loss spectrometry (EELS) in the TEM is a powerful tool for the study of electronic structure and bonding in materials. Focused probe techniques yield information at high spatial resolutions, and are therefore indispensable for the study of interfaces, where electronic structure can vary dramatically at the atomic scale. In this study, EELS in the TEM is used to directly assess the nature of bonding at Ni-SiO<sub>2</sub> interfaces in thin films. Quantitative analysis of Ni  $L_{2,3}$  edges yields information about electron filling of metal atom d-bands at the interface and in the bulk of the film. Significant changes in Ni d-band occupancy are observed between bulk and interfacial locations, and can be explained by reference to Ni-O and Ni-Si bonding at the interface. NiO formation has been identified by characteristic near-edge structure preceding the O K edge threshold in interface spectra, and by quantification of Ni white lines, revealing a charge transfer of 1.1 electrons away from the d-bands of interfacial Ni atoms. White line studies of interfacial Ni  $L_{2,3}$  spectra also demonstrate varying degrees of charge transfer to Ni atom d-bands, suggesting some form of nickel silicide formation at the interface. Large variations in the measured charge transfer from Si to interfacial Ni atoms are attributed to local fluctuations in chemistry along the

interface. These results shed new light on proposed metal-support interactions in Ni-SiO<sub>2</sub> catalysts.

#### 11:15 AM Q6.8

EPITAXY AND ATOMIC STRUCTURE DETERMINATION OF Au/TiO<sub>2</sub> INTERFACES BY COMBINED EBSD AND HRTEM. Frederic Cosandey, Dept. of Ceramic and Materials Engineering, Rutgers University, Piscataway, NJ; Pierre Stadelmann, Centre Interdepartemental de Microscopie Electronique, Ecole Polytechnique Federale de Lausanne, Lausanne, SWITZERLAND.

The Au/TiO<sub>2</sub> system is of importance in catalysis, because of its high activity for low temperature oxidation of CO and its good sensitivity as CO gas sensor. This is caused in part by a unique yet unknown synergistic effect between Au islands and TiO<sub>2</sub>. The effect of substrate temperature on epitaxial orientation relationship of Au islands on TiO<sub>2</sub>(110) substrate has been determined by high spatial resolution electron backscatter diffraction (EBSD). In addition, we have examined the atomic structure and chemistry of Au/TiO<sub>2</sub> interfaces by high resolution transmission electron microscopy (HRTEM). Upon increasing growth temperature from 300K to 775K, the epitaxial orientation relationship of Au islands on TiO<sub>2</sub>(110) changes from (111)Au to (11-2)<sub>Au</sub> plane orientation with the same <110><sub>Au</sub>//[001]TiO<sub>2</sub> direction. In both cases, two epitaxial variants are observed. The Au/TiO<sub>2</sub> interfacial structure and chemistry of these two epitaxial orientations has been determined by HRTEM. The epitaxial orientation results are explained in terms of stoichiometry of TiO<sub>2</sub>(110) interface and Ti-Au interfacial bonds.

#### 11:30 AM Q6.9

THEORETICAL EXPLANATION OF PT TRIMERS OBSERVED BY Z-CONTRAST STEM. Karl Sohlberg, Sokrates T. Pantelides\* and Stephen J. Pennycook\*, Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN; \*also: Department of Physics and Astronomy, Vanderbilt University, Nashville, TN.

First-principles quantum-mechanical calculations on  $\gamma$ -alumina have revealed a fascinating "reactive sponge" phenomenon.  $\gamma$ -alumina can store and release water, but in a unique, "reactive" way. This "reactive sponge process" facilitates the creation of aluminum and oxygen vacancies in the alumina surface. Earlier atomic-resolution Z-contrast STEM images of ultradispersed Pt atoms on a  $\gamma$ -alumina support showed the individual atoms to form dimers and trimers with preferred spacings and orientations that are apparently dictated by the underlying support. [Nellist and Pennycook, *Science*, **274**, 413 (1996).] In turn, the reactive sponge property of  $\gamma$ -alumina is the key to understanding the Pt clusters. Our calculations demonstrate that if three Pt atoms fill three vacancies created during the reactive sponge process, the resulting geometry precisely matches that of the Pt trimers observed in the Z-STEM images. Understanding the initial nucleation of small clusters on the complex gamma alumina surface is an essential first step in determining the origins of catalytic activity.

#### 11:45 AM Q6.10

THE CHARACTERIZATION OF ULTRADISPERSED CATALYSTS USING HREM AND MOLECULAR DYNAMICS. M. José-Yacamán<sup>1,2</sup>, S. Tehuacanero<sup>1</sup>, L. Rendón<sup>1</sup>, L. González-Tovany<sup>2</sup>, M. Fernández<sup>2</sup> and J.A. Ascencio<sup>2</sup>; <sup>1</sup>Instituto de Física, Universidad Nacional Autónoma de México, México, MÉXICO; <sup>2</sup>Instituto Nacional de Investigaciones Nucleares, México, MÉXICO.

One of the outstanding problems in catalysis is the understanding of catalysts which are characterized by chemical methods as ultradispersed (100% dispersion). In other words in those catalysts all the active atoms are accessible for the chemical reactions. However traditional TEM fail to show a structure consistent with the chemisorption data.

In the present work we study the case of Pt- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysis which is widely used in reforming in naphthes. We used molecular dynamics simulations and quantum mechanics approximations to study the structure of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and the interaction of Pt atoms with the vacancies on the alumine. The resulting model was used to simulate HREM of images of the particle structure. These simulations provide a guide to understanding the structure of the Pt clusters. In particular it became clear the role of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> which acts as a Supersponge and the formation of clusters inside the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> matrix.

### SESSION Q7: INTERFACES IN METALS AND CERAMICS I

Chairs: Robert J. Gottschall and Robert Hull  
Thursday Afternoon, December 2, 1999  
Salon A/B (M)

#### 1:30 PM \*Q7.1

THE USE OF THE FOCAL-SERIES RECONSTRUCTION

TECHNIQUE IN HRTEM FOR SOLVING MATERIALS PROBLEMS. A. Thust, C.L. Jia, Forschungszentrum Jülich GmbH, Institut für Festkörperforschung, Jülich, GERMANY.

Modern high-resolution electron microscopes achieve routinely a resolution near 1 Angstrom. However, due to the nonlinear properties of imaging and due to optical aberrations, the images made with such microscopes can no longer be interpreted intuitively. This is especially the case for the latest generation of microscopes equipped with field emission guns. Since image simulation as a classical interpretation aid is strongly restricted concerning its applicability and its efficiency, new techniques are developed which offer again a more direct insight into the observed object. Such techniques are the correction of the spherical aberration, electron holography and focal-series reconstruction. In the framework of focal-series reconstruction one calculates numerically the quantum mechanical electron wave function at the exit plane of the object, using approximately 20 images taken from the same object area with different settings of the objective lens defocus. Recent applications of the focal-series reconstruction technique to various materials systems, reaching from semiconductors via ceramics to metallic alloys offer a direct insight into atomic details, which has not been reached so far by other techniques.

#### 2:00 PM Q7.2

APPLICATION OF QUANTITATIVE HREM IN PERFECT CRYSTAL AND INTERFACE STRUCTURE DETERMINATION. V. Radmilovic, R. Kilaas, and U. Dahmen, National Center for Electron Microscopy, Lawrence Berkeley Laboratory, University of California, Berkeley, CA.

Over the last few years much progress has been made in the field of quantitative image comparison and automatic structure determination/refinement in HRTEM. This work is an attempt to further refine and integrate these tools and to apply these techniques to the study of the Al<sub>2</sub>CuMg intermetallic phase. The structure of the Al<sub>2</sub>CuMg precipitate in an Al matrix has been determined by using a combination of image processing, quantitative comparison between experimental and theoretical images, and automatic refinement of imaging and structural parameters. Similarly, applying the same quantitative methods to experimental images of interface structures between the Al-based matrix and Al<sub>2</sub>CuMg precipitates resulted in good agreement between experiment and theory. In the Al-Cu-Mg based alloys investigated, two distinct precipitate morphologies are observed. Both are laths elongated along <100> directions common to the matrix and the precipitate and both lie on {021} planes of the matrix. The difference between the two types of precipitates is discussed in terms of their lattice correspondence, and type II precipitates are shown to follow an invariant line strain. Moiré analysis of lattice distortions reveals that {020} Al planes remain undistorted while {002} Al planes suffer significant shear during S-phase nucleation. This work is supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-ACO3-76SF00098.

#### 2:15 PM \*Q7.3

QUANTITATIVE MAPPING OF CONCENTRATIONS AND BONDING STATES BY ENERGY FILTERING TEM. Joachim Mayer, Jürgen Pitzko, and Jan Marien, Max-Planck-Institut für Metallforschung, Stuttgart, GERMANY.

We have developed new methods to quantify the data acquired by electron spectroscopic imaging (ESI) in an energy filtering TEM. The analysis is based on recording series of energy filtered images across inner shell loss edges or in the low loss region. From the series of ESI images, electron energy loss (EEL) spectra can be extracted and subsequently analysed using standard EELS quantification techniques. From an ESI series we can now measure the absolute amount (area density) of an element in the given sample area or the concentration ratios of one element with respect to other elements. From a series of ESI images in the low-loss region, accurate values of the specimen thickness can be obtained, provided the mean free path for inelastic scattering is known. Spectrum line-profiling has been shown to be an efficient way to acquire and present the information on the chemistry of an interface. The present investigations comprise results which have been obtained on two different EFTEMs, a Zeiss EM 912 Omega and the new JEOL 2010 FEF. The systems studied include grain boundary films in Si<sub>3</sub>N<sub>4</sub>, Cu/Al<sub>2</sub>O<sub>3</sub>-interfaces with Ti interlayers and semiconductor metallisation layers. The results show that segregation in the submonolayer range can still be analysed with high spatial resolution. For the study of the energy loss near edge structure (ELNES) a higher energy resolution is required in order to extract reliable information on the bonding. A new microscope project will be introduced, which will make it possible to reach an energy resolution of 0.2 to 0.3 eV.

#### 2:45 PM Q7.4

COMBINED HRTEM AND EFTEM STUDY OF PRECIPITATES IN TUNGSTEN AND CHROMIUM DOPED TiB<sub>2</sub>. Werner Mader, Bert Freitag, Institut für Anorganische Chemie der Universität Bonn, GERMANY; Rainer Telle, Clemens Schmalzried, Institut für Gesteinshüttenkunde, RWTH Aachen, GERMANY.

Precipitation in supersaturated mixed crystals of transition metal borides in the system Ti<sub>2</sub>-WB<sub>2</sub>-CrB<sub>2</sub> leads to particle-strengthened hard materials. The structure and chemical composition of two types of precipitates in the hexagonal TiB<sub>2</sub> matrix were studied by means of high-resolution TEM and energy filtering TEM using a 300keV high-resolution electron microscope (CM300UT-FEG) fitted with a Gatan imaging filter. Type I particles (W<sub>2</sub>B<sub>5</sub> structure) are precipitated at the basal plane whereas type II precipitates are thin platelets (thickness 0.8 nm) lying parallel to the {1100} prism planes. Lattice images yield precipitate thickness and lattice displacements of the metal positions with respect to the matrix, which uniquely depends on the precipitate thickness of the W<sub>2</sub>B<sub>5</sub> particles. Valuable information on the chemical composition at high lateral resolution is obtained from elemental maps of all chemical constituents using electron spectroscopic imaging (ESI). The type II precipitates show a decrease in the B and Ti concentration, whereas the W concentration increases and the Cr is homogeneously distributed. The HRTEM results combined with the results of the elemental maps can be explained by a structural model based on the intergrowth of the  $\beta$ -WB structure in the TiB<sub>2</sub> matrix. Quantitative EDS analysis of the type II precipitates results in a W and Ti concentration of the same amount, hence the stoichiometry of type II is W<sub>0.5</sub>Ti<sub>0.5</sub>B. The double deficient boron layers in W<sub>0.5</sub>Ti<sub>0.5</sub>B with a spacing of 0.38 nm can be used to examine the resolution limit of ESI: In the boron jump-ratio image of W<sub>0.5</sub>Ti<sub>0.5</sub>B two dark lines are clearly resolved indicating the deficient boron layers. The chemical origin of that contrast is critically discussed.

#### 3:30 PM \*Q7.5

CHARACTERIZATION OF AMORPHOUS FILMS IN METAL MATRIX COMPOSITES. George C. Weatherly, McMaster University, Dept of Materials Science and Engineering, Hamilton, ON, CANADA.

In many Al- or Mg- based metal matrix composites, reinforced with SiC, Si<sub>3</sub>N<sub>4</sub> or Al<sub>2</sub>O<sub>3</sub>, a thin (1-2nm) amorphous film is commonly observed at the interface between the matrix and the reinforcing phase. In SiC or Si<sub>3</sub>N<sub>4</sub> reinforced systems, the Si-rich amorphous phase is formed from the precursor (natural) oxide film at the surface of the SiC and Si<sub>3</sub>N<sub>4</sub>. However with Al<sub>2</sub>O<sub>3</sub> reinforcement, an amorphous phase only forms when certain key alloying elements (Si, Mg and Sr) are present in the Al alloy matrix. In this presentation I will highlight the role of analytical electron microscopy in unravelling the structure and composition of the films, using a JEOL 2010 FEG electron microscope. The composition of the films has been determined by EDX and EELS methods. The latter technique is also useful for identifying the nature of the Si - O coordination in the amorphous phase. HRTEM has been used to measure the thickness of the films and to study the "wetting" characteristics of the amorphous phase at the junction of two reinforcing particles. For Al<sub>2</sub>O<sub>3</sub> reinforced alloys, Sr additions to the base alloy are shown to be critical to nucleate the amorphous phase.

#### 4:00 PM Q7.6

HIGH SPATIAL RESOLUTION X-RAY MICROANALYSIS OF RADIATION-INDUCED SEGREGATION IN PROTON-IRRADIATED STAINLESS STEELS. Edward A. Kenik, Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, TN; Jeremy T. Busby, Gary S. Was, Nuclear Engineering and Radiological Sciences Dept., University of Michigan, Ann Arbor, MI.

Irradiation-assisted stress corrosion cracking (IASCC) of neutron-irradiated austenitic alloys has been attributed in part to radiation-induced segregation of both major and minor alloying elements near point defect sinks, especially grain boundaries. As a result of the low irradiation temperature (<570 K), the segregation profiles are very narrow (<5 nm) and require the high spatial resolution of a field emission gun scanning transmission electron microscope (FEG-STEM). Energy-dispersive spectrometry spectrum lines have been utilized to characterize both pre-irradiation segregation associated with prior heat treatment and radiation-induced segregation produced by proton-irradiations used to simulate neutron irradiation. The segregation evolves from Cr- and Mo-enrichment at grain boundaries prior to irradiation to W-shaped Cr profiles at ~1 dpa (displacement per atom) to traditional Cr depletion profiles with increasing dose. This redistribution is accompanied by Si, Ni, and P enrichment at grain boundaries. The impact of pre-irradiation segregation on subsequent RIS and the role of RIS on IASCC will be discussed. Research sponsored in part by U.S. Department of Energy, Division of Materials Sciences, under contract DE-AC05-96OR22464 with Lockheed Martin Energy

Research Corp. and through the SHaRE User Program under contract DE-AC05-76OR00033 the Oak Ridge Institute for Science and Education. Research in part utilized the Shared Research Equipment (SHaRE) User Facilities at Oak Ridge National Laboratory.

#### 4:15 PM Q7.7

SUBSTITUTIONAL IMPURITY SEGREGATION TO THE  $\Sigma 5(310)/[001]$  STGB IN FCC METALS. Juergen M. Plitzko, Geoffrey H. Campbell, Wayne E. King, Chemistry and Materials Science Directorate, University of California, Lawrence Livermore National Laboratory, Livermore, CA; Stephen M. Foiles, Computational Materials Science Department, Sandia National Laboratories, Livermore, CA.

Investigations of the  $\Sigma 5$  symmetric tilt grain boundaries (STGB) in face-centered cubic (FCC) metals in four different metal systems were performed. The metals we have chosen include pure Aluminum, pure Copper, Copper with 1at% Silver, and Aluminum with 1at% Copper. The model grain boundaries have been fabricated with ultra-high vacuum diffusion bonding of single crystals. The atomic structure of the Sigma 5 (310)/[001] STGB for the different metal systems was modeled with atomistic potentials based on the Embedded Atom Method (EAM). The theoretical calculations of the interface structure indicates that the Cu and the Ag atoms segregate to distinct atomic sites at the interface. High resolution electron microscopy (HRTEM) and analytical electron microscopy including electron energy loss spectroscopy and x-ray energy dispersive spectrometry have been used to prove the predictions of the EAM model. The HRTEM images and the analytical measurements were performed using a Philips CM30 FEG equipped with an imaging energy filter. The amount of the segregated species at the interface was quantified. To determine the atomic positions of the segregated atoms at the interface, HRTEM coupled with image simulation and reconstruction of through-focal series have been used. Finally, these experimental results are discussed and compared to the theoretical model. This work was performed at Lawrence Livermore National Laboratory under the auspices of the US Dept. of Energy under Contract W-7405-Eng-48

#### 4:30 PM Q7.8

STEM ANALYSIS OF THE SEGREGATION OF Bi TO  $\Sigma 19$  GRAIN BOUNDARIES IN Cu. Wilfried Sigle, Li-Shin Chang, Wolfgang Gust, Manfred Rühle, Max-Planck-Institut für Metallforschung, Stuttgart, GERMANY.

The Cu(Bi) system has traditionally been a model system for the study of grain boundary (GB) segregation. It is well known that the Bi segregation leads to a reduction of the GB adhesion. This is often accompanied by a faceting of the GB. The amount of segregation was shown to increase with GB energy [1]. Only recently the phase diagram on the Cu-rich side of the phase diagram has been established [2]. This allows it to perform systematic studies of the segregation phenomenon. By an Auger study in polycrystalline Cu strong evidence was found for pre-wetting of GBs within the one-phase regime of the volume phase diagram [3]. In the present work segregation at a specific high-energetic GB ( $\Sigma 19$ ) was studied using transmission electron microscopy (TEM) and scanning TEM. Whereas TEM enables us to characterize the GB microstructure, STEM is used to measure the amount of Bi segregated to the boundary [1]. The Cu bicrystals were prepared both by the Bridgman technique and by diffusion bonding. They were doped by various amounts of Bi thus covering a wide range within the phase diagram. It is found that the segregation strength as well as the tendency for faceting depends sensitively on the doping conditions. In particular GBs doped within the pre-wetting regime exhibit exceptionally high Bi concentrations, are strongly faceted and mechanically extremely brittle. The observations will be discussed in the context of earlier results. [1] U. Alber, H. Müllejans, and M. Rühle, to be published in Acta Mater. [2] L.-S. Chang, B.B. Straumal, E. Rabkin, W. Gust, and F. Sommer, J. Phase Equilibria 18 (1997) 128. [3] L.-S. Chang, E. Rabkin, B. Straumal, P. Lejcek, S. Hofmann, and W. Gust, Scripta Mater. 37 (1997) 729.

#### 4:45 PM Q7.9

MEASUREMENT OF THE ATOMIC STRUCTURE OF BISMUTH DOPED COPPER  $\Sigma 5$  GRAIN BOUNDARIES. Thomas Gemming, Uwe Alber, Manfred Rühle, Max-Planck-Institut für Metallforschung, Stuttgart, GERMANY.

The phenomenon of embrittlement of copper due to the segregation of bismuth is well known for more than 100 years. Nevertheless a complete atomistic understanding of the underlying principles is still not achieved. To investigate the influence of structural changes we used quantitative high resolution electron microscopy (QHREM) to investigate copper grain boundaries with atomic resolution. We analyzed the structure of  $\Sigma 5(013)[100]$  grain boundaries in pure as well as in bismuth doped copper. HREM using the JEOL ARM1250 installed in Stuttgart allows an atomically resolved phase contrast

image of a copper  $\Sigma 5$  grain boundary which makes it possible to reliably analyze the geometric structure. Quantitative analysis of the experimental images involving HREM image simulations reveals the position of specific atom columns at the grain boundary. The subtle differences of the structure of doped as well as clean boundaries can therefore be analyzed. Using analytical electron microscopy (STEM) the amount of Bismuth segregation was measured to get a complementary measurement of the chemistry of the interface. The combination of chemical and structural results gained from electron microscopy give a complete picture of the investigated grain boundary. The slight structural changes originating from a segregation of about 1.5 Bi-atoms/nm<sup>2</sup> to the  $\Sigma 5$  grain boundary will be reported. These results can be related to the physical properties of bismuth doped copper.

SESSION Q8: POSTER SESSION:  
PARTIALLY ORDERED AND NANOPHASE  
MATERIALS

Chairs: Colin Peter Flynn and Mehmet Sarikaya  
Thursday Evening, December 2, 1999  
8:00 P.M.  
Exhibition Hall D (H)

**Q8.1**

LOW DOSE HREM IMAGING OF LATTICE CURVATURE IN TWISTED MPDI POLYMER CRYSTALS. Christian Kuebel, Daniel P. Lawrence and David C. Martin, The University of Michigan, Materials Science and Engineering, Ann Arbor, MI.

Poly(m-phenylene diisophthalamide) (MPDI) is an all-aromatic polyamide used to manufacture thermally stable fibers (Nomex by DuPont). When MPDI-DMAc solutions are slowly crystallized by exposure to a non-solvent (water) in a diffusion vessel, the polymer precipitates into uniform, regularly twisted crystalline bundles. Here, we examine the internal structure of this remarkable morphology at high resolution. HREM images have been obtained for planes both parallel and nominally perpendicular to the axis of the twisted crystal bundle. The lattice planes show regular, extensive local bending, indicating that the twisted morphology leads to large local distortions of the crystal lattice. Electron diffraction patterns reveal a symmetry that is substantially different from that of the model proposed by Kakida et al. (1976) for the commercially spun MPDI fiber. Computer generated models for the crystal structure will be shown and compared with the available experimental TEM and SAED data.

**Q8.2**

ELEMENT COMPOSED IMAGING OF NANO SOLIDS IN SOLUTION. Jan-Olov Bovin, Gunnell Karlsson, Jan-Olle Malm, Olivier Balmes, Torsten Huber, National Center for HREM and the Biomicroscopy Unit, Chemical Center, Lund University, Lund, SWEDEN.

The preparation of frozen amorphous thin films of solutions containing crystals, and imaging with cryo energy filtered TEM, opens for the first time the possibility to image the chemistry of solids interacting with liquids. The future possible areas of research include: dynamic of crystal growth processes, adsorption mechanisms, ion exchange, structure determination of solids in equilibrium with solutions, etc. Vitrification of the liquid phase, on the TEM grid, was achieved by plunging it into liquid ethane. The vitrified specimen was transferred into the microscope by an Oxford CT3500 cryo-holder. The specimen temperature was kept below -183°C. The vitrified films, including the crystals, should have a thickness of about 200 nm or preferably less. The Philips CM120 BioTWIN Cryo, here used for cryo-TEM, has a focal length of 6 mm and a structural resolution of 0.4 nm. The information content of the inelastically scattered electrons can be used to record jump ratio elemental maps in less than a minute. This is shown here, for the first time, using a post column AutoFilter GIF100. Several preliminary investigations of solids in solution will be presented. The aggregation of 18 nm palladium colloids in water solution was studied and it was found that jump ratio maps could be recorded from the same area and the twin-defects indicate an image-resolution of about 2.5 nm. It is shown that it is also possible to freeze thin films of methanol, ethanol and tetrahydrofurane (THF). It was found that frozen methanol was more stable than ice and a new type of aggregation (sponge like) of 2.5 nm Ru clusters was identified in THF. In a mixture of gold and palladium colloids the different elements could be identified using two jump ratio images recorded at the palladium M-edge and the N-edge of gold.

**Q8.3**

ION IMPLANTED AMORPHOUS SILICON STUDIED BY VARIABLE COHERENCE TEM. Murray Gibson, Argonne National Lab, Materials Science Div, Argone, IL; Ju-Yin Cheng, Paul Voyles, Univ of Illinois, Dept of Physics and Materials Science, Urbana, IL;

Michael Treacy, NEC Research Inst, Princeton, NJ; D.C. Jacobson, Lucent Bell Lab, Murray Hill, NJ.

Amorphous silicon formed by ion-implantation of crystalline silicon is investigated with the use of VCTEM (variable-coherence transmission electron microscopy). This technique is sensitive to medium-range-order structure. The results on as-implanted samples showed a striking similarity of evaporated amorphous silicon. We found that both ion-implanted and evaporated samples have paracrystalline structures, rather than continuous random-network structures. We are also interested in the structure-relaxation behavior of the ion-implanted amorphous silicon after in-situ and ex-situ thermal annealing. We expect that the structure will tend to form a continuous random network due to heat release during annealing, and plan to report results at the meeting. Modeling of the structural relaxation will also be covered in the paper.

**Q8.4**

BONDING IN ION-IMPLANTED CARBON FILMS CHARACTERIZED BY TEM SPECTRUM LINES AND ENERGY-FILTERED IMAGING. James Bentley, Oak Ridge National Laboratory, Oak Ridge, TN; Kevin C. Walter, Los Alamos National Laboratory, Los Alamos, NM (now at Southwest Research Institute, San Antonio, TX); Neal D. Evans, Oak Ridge Institute for Science and Education, Oak Ridge, TN.

The electrical, mechanical, and electrochemical properties of diamond-like carbon (DLC) coatings are determined by the amount of sp<sup>3</sup> bonding. Correlations of bonding and properties are important for optimizing coatings for specific applications. Cross-sectioned TEM specimens of DLC thin films that have been ion implanted after plasma deposition have been studied. Ratios of sp<sup>2</sup>/sp<sup>3</sup> bonding have been measured from electron energy-loss spectra (EELS) with established methods that are based on the relative intensities of  $\pi^*$  and  $\sigma^*$  features at the carbon K-edge. To avoid changes in sp<sup>2</sup>/sp<sup>3</sup> ratio by beam damage that can be encountered with focussed probes, high-spatial-resolution spectrum lines were acquired in the TEM mode with a Gatan imaging filter (GIF) interfaced to a Philips CM30. The method employs a simple slit in the GIF entrance aperture and the use of a specimen rotation holder. N-implantation results in increased sp<sup>2</sup> bonding and a 1.3 eV shift to higher binding energies. No shift was observed in Ar-implanted material. Also, the fraction of implanted species retained is much smaller for Ar than for N. The results will be discussed with reference to chemical reactions. Preliminary results have also been obtained for energy-filtered TEM mapping of the  $\pi^*$  to  $\sigma^*$  ratio. Nominally 3eV-wide slits were used to acquire an extended set of energy-filtered images at the carbon K-edge. Custom scripts for DigitalMicrograph software were developed to process the data. Research at the ORNL SHaRE User Facility was supported by the Division of Materials Sciences, U.S. Department of Energy under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corp., and through the SHaRE Program under contract DE-AC05-76OR00033 with Oak Ridge Associated Universities.

**Q8.5**

ATOMIC-SCALE STRUCTURAL INVESTIGATIONS ON THE DIRECT NUCLEATION OF CUBIC BORON NITRIDE FROM SP<sup>3</sup>-HYBRIDIZED AMORPHOUS BORON NITRIDE UNDER HIGH PRESSURES AND TEMPERATURES. J.Y. Huang, Research Center for Ultra-High Voltage Electron Microscopy (UHVM), Osaka University, Osaka, JAPAN; National Institute for Research in Inorganic Materials, Tsukuba, JAPAN; H. Mori, UHVM, Osaka University, Osaka, JAPAN.

By controlling the microstructure of the starting materials, i.e. by ball-milling a commercial hexagonal boron nitride (h-BN) to an amorphous boron nitride (a-BN), the subsequent high-pressure and high-temperature (HP-HT) induced phase transformation has been significantly facilitated. Namely cubic boron nitride (c-BN) forms at 900 °C and achieves accomplishment at 1350 °C under 7.7 GPa, which are significantly less- extreme conditions than that of crystalline h-BN under similar HP-HT treatments. HRTEM and EELS clarified the nucleation mechanism at an atomic scale. It demonstrated that the c-BN phase nucleates directly from the sp<sup>3</sup> hybridized amorphous matrix, which is originally induced by ball milling and is therefore responsible for the reduced HP-HT conditions. This c-BN nucleation mechanism is completely different from the so-called diffusionless puckering mechanism, but very similar to one of the proposed mechanisms involved in the chemical vapor deposition (CVD) of diamond and c-BN. The present experimental results may provide not only a less- extreme way to synthesize nanocrystalline c-BN material but also key clues to the understanding of the nucleation mechanisms involved in the CVD diamond or c-BN, which are still under controversy.

**Q8.6**

ENERGY-FILTERED TEM IMAGING AND PEELS ANALYSIS OF

**BORON NITRIDE AND CARBON NANOTUBES.** Oleg Lourie, Rodney S. Ruoff, Dept of Physics, Washington Univ, St. Louis, MO; Bart Bartlett, Carolyn Jones, William E. Buhro, Dept of Chemistry, Washington Univ, St. Louis, MO; Thomas F. Kelly, Dept of Materials Science and Engineering, Univ of Wisconsin, Madison, WI.

Carbon nanotubes are being developed for a range of applications that take advantage of their unique properties. Like carbon, boron nitride forms both hexagonal and tetrahedrally-coordinated structures and is known in arc synthesis to form nanotubes. Chemical-vapor-deposition synthesis of nominally pure C and BN nanotubes has produced material, which has been surface-analyzed by x-ray photoelectron spectroscopy and Auger electron spectroscopy for elemental composition. These nanotubes have also been studied with energy-filtered TEM imaging and parallel electron energy loss spectroscopy to determine if the nanotubes are indeed composed of boron and nitrogen. Results of this work will be presented. These efforts are aimed at producing extremely pure boron nitride nanotubes and assessing the character of the chemical bonding.

#### **Q8.7**

**ANALYTICAL HIGH RESOLUTION TEM STUDY OF THE Au/TiO<sub>2</sub> CATALYST.** Tomoki Akita, Koji Tanaka, Susumu Tsubota, Masatake Haruta, Osaka National Research Institute, AIST, Osaka, JAPAN.

Gold has been known to be chemically inert, however, it shows remarkably high activity as a catalyst when finely dispersed with a diameter smaller than 10nm on a metal oxide support. Especially, interesting features have been observed in Au/TiO<sub>2</sub> systems. The selective oxidation of propylene to propylene oxide occurs only on anatase TiO<sub>2</sub> support, but not on rutile TiO<sub>2</sub>. The reaction switches from epoxidation to hydrogenation depending on the size of Au particles in the system of propylene in the presence of hydrogen and oxygen. Details of above characteristic behavior are not clearly understood.

We have studied the crystal structure and electronic structure of the Au/TiO<sub>2</sub> catalyst by HR-TEM, EELS and HAADF-STEM. Some basic feature was found. There was a preferential orientation between Au particles and anatase TiO<sub>2</sub>, but not with rutile TiO<sub>2</sub>. This orientation relationship was consistent with the result predicted from geometrical calculation. EELS measurement was also done for OK-edge ELNES. Specific features induced by Au particles supported were not found yet. But the shapes of EELS spectra from TiO<sub>2</sub> supports used for catalyst were different from the standard spectra obtained from single crystal. This difference might be attributed to the degree of crystallinity. The shapes of Au particles were also estimated from the intensity of Z-contrast images. The intensities of Au particles will show D<sup>3</sup> dependence on the diameter D of Au particles, however, those of some particles were weaker than the predicted value obtained from D<sup>3</sup> dependence. It might be suggested that those particles had raft-like structure.

#### **Q8.8**

**LOW VOLTAGE AND HIGH RESOLUTION SEM IMAGING AND MICROANALYSIS OF INDUSTRIAL SUPPORTED CATALYSTS.** Jingyue Liu, Monsanto Corporate Research, Monsanto Company, St. Louis, MO.

The use of a high-brightness field-emission gun and high-resolution probe-forming lenses coupled with a novel secondary electron detection system makes it possible to acquire nanometer-resolution surface images of bulk materials at low voltages. The advantages of low voltage SEM include enhanced surface sensitivity, reduced sample charging for non-conducting materials, reduced sample damage, and significantly reduced electron range and interaction volume. Because of the fall of electron range and the corresponding reduction in interaction volume, low voltage microanalysis can provide compositional information of bulk samples with enhanced surface sensitivity and significantly improved spatial resolution, especially for analysis of high atomic number particles dispersed on light-element supports. The tremendous decrease of the interaction volume at low voltages enhances our ability to detect and subsequently analyze the chemical composition of nanoparticles in supported catalysts and other heterogeneous materials. The recent advancement in low voltage SEM imaging and microanalysis and the application of these techniques to the study of industrial supported catalysts will be discussed.

#### **Q8.9**

**ON-PARTICLE EDS ANALYSIS OF BIMETALLIC, CARBON-SUPPORTED CATALYSTS.** Deborah L. Boxall, Charles M. Lukehart, Vanderbilt University, Department of Chemistry, Nashville, TN; Ed A. Kenik, Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, TN.

It has been determined by several research groups that the inclusion of a secondary alloying metal in platinum-based heterogeneous

catalysts can result in improved catalytic activity and/or longevity. The preparation of bimetallic catalysts with specific metal:metal ratios and the appropriate surface composition for maximum activity has therefore become an active area of research. It is possible to prepare bimetallic, carbon-supported metal catalysts by thermally treating carbon impregnated with a single-source, heterometallic molecular precursor. Through judicious control of the thermal treatment conditions, bimetallic catalysts with the same overall metal:metal ratio as that initially present in the molecular precursor can be obtained. High resolution TEM coupled with energy dispersive spectroscopy allows the elemental composition of individual metal particles with diameters as small as 1nm to be determined. While the results from several different bimetallic catalysts indicated that there is some compositional size dependence, this dependence is consistent with loss of a volatile oxide species from the surface of the metal particles. Application of a mathematical model to compensate for this presumed material loss results in calculated average metal:metal ratios within experimental error of those measured by bulk chemical analysis.

#### **Q8.10**

**HREM AND QUANTUM MECHANIC ANALYSIS OF THIOL MOLECULES AND THEIR INFLUENCE IN GOLD NANOPARTICLES BEHAVIOR.** J.A. Ascencio, M. Jose-Yacamán, Instituto Nacional de Investigaciones Nucleares. MEXICO.

Since the different efforts to generate nanostructured self assembled arrays, there have been multiple methods to produce them. From systems using DNA molecules to the application of n-alkyl thiols, the passivated and arranged nanoparticles have been obtained successfully, however there is not enough knowledge about the behavior of the thiols molecules around the metal particles. In several reports we have shown partial results of HREM simulation as a tool to interpret images produced experimentally, and this work use that method to analyze more carefully the role of the thiol molecules. By applying high resolution electron microscopy observation and simulation techniques, both classical and quantum mechanics based, an analysis is made to identify the molecular properties, charge distribution and direct influence over the dynamic or ordering phenomenon. Density Functional Theory based calculation and molecular dynamics is applied to support theoretically the observations of HREM of well defined structures of gold nanoparticles produced by the method developed by Brust. The HREM observations showed structural fluctuation and preferences for orientations which must be directly influenced by the distribution of thiols around the particle and how these molecules are affected when the electron beam is concentrated.

SESSION Q9: POSTER SESSION:  
INTERFACES IN METALS AND CERAMICS  
Chairs: Ian M. Anderson, Nigel D. Browning and  
George C. Weatherly  
Thursday Evening, December 2, 1999  
8:00 P.M.  
Exhibition Hall D (H)

#### **Q9.1**

**CHARACTERIZATION OF THE INTERFACE BETWEEN SAPPHIRE AND HEXA-ALUMINATE BY EXIT WAVE RECONSTRUCTION.** B. Wessler, A. Steinecker, W. Mader, Universitaet Bonn, Bonn, GERMANY.

Epitaxial thin films of rare-earth hexa-aluminates on basal plane sapphire have been obtained by chemical solution deposition. Polycrystalline films consisting of the intermediate phase LnAlO<sub>3</sub> (Ln: La<sup>3+</sup>, Nd<sup>3+</sup>) convert into LnAl<sub>11</sub>O<sub>18</sub> at temperatures  $\geq 1500$  ° C by reaction with the underlying substrate leading to extremely smooth films. LnAl<sub>11</sub>O<sub>18</sub> films, better described by the formula Ln<sub>1-x</sub>Al<sub>12-y</sub>O<sub>19-z</sub>, with magnetoplumbite structure grow with (0001)mp || (0001)s out-of-plane and [11 $\bar{2}$ 0]mp || [10 $\bar{1}$ 0]s in-plane orientation relationship. The magnetoplumbite structure consists of spinel-structure blocks with interlayers containing Ln. To determine the terminating layer at the interface exit wave reconstruction by means of focus series was carried out using a field emission TEM. Due to the inversion of the imaging process major artefacts at the interface can be eliminated, and therefore the obtained information is more reliable than the analysis of HRTEM "single shots". Exit waves were simulated based on different models of interfaces and were compared with the reconstructed waves to localize the interface and the first layer containing Ln within the hexa-aluminate. Thus it was found that the hexa-aluminate is terminated by a layer within the spinel block adjacent to the terminating sapphire layer, which is discussed in relation to the epitaxial system (111) spinel || (0001) sapphire.



### Q9.2

ATOMIC AND ELECTRONIC STRUCTURE ANALYSIS OF  $\Sigma=3$ , 9 AND 27 BOUNDARY, AND MULTIPLE JUNCTION IN  $\beta$ -SiC. Koji Tanaka and Masanori Kohyama, Osaka Natl. Res. Inst., Dept. of Material Physics, Osaka, JAPAN.

It is very powerful to combine high-resolution electron microscopy (HREM) and theoretical calculation (tight-binding and *ab-initio*) for the grain boundary research. The structures of  $\Sigma=3$ , 9 and 27 boundary, and triple and quadruple junction in  $\beta$ -SiC were studied by HREM and theoretical calculation. Especially, the existence of the variety of structures of  $\Sigma=3$  incoherent twin boundary and  $\Sigma=27$  was shown by HREM.

The structure of  $\Sigma=3$  incoherent twin boundary consists of an array of structural units and the array changes its features depending on its length or circumstances. The array is comprised of aligned symmetrical structural units which are composed of 5, 7, and 6 membered rings in this order at short boundary, both symmetrical and asymmetrical structural units at middle boundary, and zigzag or obliquely distributed symmetrical structural units at long boundary. It is known from tight-binding calculation that the grain boundary energy becomes lower when Si is reconstructed than when C is reconstructed and the energy difference between the symmetrical 5-7-6 membered rings structural unit and the asymmetrical one is not so large, and then both structures can occur.

$\Sigma=27$  boundary can change its structure from straight to zigzag continuously by shifting the position of boundary. This type of boundary position shift also occurs at multiple junctions instead of a rigid body translation. EELS analysis was also applied to investigate a bonding state at the boundary. The detail of a comparison between HREM observation and theoretical calculation will be discussed.

### Q9.3

ELECTRONIC EFFECTS ON GRAIN BOUNDARY STRUCTURE IN BCC METALS. Geoffrey H. Campbell, Wayne E. King, James Belak, John A. Moriarty, University of California, Lawrence Livermore National Laboratory, Livermore, CA; Stephen M. Foiles, Sandia National Laboratories, Livermore, CA.

The dominant factor in determining the atomic structure of grain boundaries is the crystal structure of the material, e.g. FCC vs. BCC. However, for a given crystal structure, the structure of grain boundaries can be influenced by electronic effects, i.e. by the element comprising the crystal. Understanding and modeling the influence of electronic structure on defect structures is a key ingredient for successful atomistic simulations of materials with more complicated crystal structures than FCC. We have found that grain boundary structure is a critical test for interatomic potentials. To that end, we have fabricated the identical  $\Sigma 5$  (310)/[001] symmetric tilt grain boundary in three different BCC metals (Nb, Mo, and Ta) by diffusion bonding precisely oriented single crystals. The structure of these boundaries have been determined by high resolution transmission electron microscopy. The boundaries have been found to have different atomic structures. The structures of these boundaries have been modeled with atomistic simulations using interatomic potentials incorporating angularly dependent interactions, such as those developed within Model Generalized Pseudopotential Theory. The differing structures of these boundaries can be understood in terms of the strength of the angular dependence of the interatomic interaction. This work was performed under the auspices of the United States Department of Energy and the Lawrence Livermore National Laboratory under contract number W-7405-Eng-48.

### Q9.4

STRUCTURAL STUDY OF A [100]45° TWIST PLUS 7.5° TILT GRAIN BOUNDARY IN ALUMINIUM BY HREM. M.Shamsuzzoha, School of Mines and Energy Development, and Department of Metallurgical and Materials Engineering, The University of Alabama, Tuscaloosa, AL; P.A. Deymier, Department of Materials Science and Engineering, University of Arizona, Tucson, AZ; David J. Smith, Center for Solid State Science and Department of Physics and Astronomy, Arizona State University, Tempe, AZ.

A [100]45° twist plus 7.5° tilt grain boundary in aluminium prepared by cold rolling and annealing has been studied by high resolution electron microscopy. The direct interpretability of the image features in terms of atomic column positions allows structural models of the grain boundary to be developed. The boundary exhibits a high concentration of steps due to the 7.5° tilt from a perfect [100]45° quasiperiodic misorientation. Occurrence of co-incidence and pseudo co-incidence of atomic planes across the interface appears to play an important role in the formation of steps along this boundary. Local relaxation of atoms resulting from the perturbation of a [100]45° twist bicrystal determines the boundary structure.

### Q9.5

ATOMIC STRUCTURE OF GOLD BOUNDARIES. C.J.D. Hetherington, Sheffield Univ, Dept of Electronic and Electrical Engineering, Sheffield, UNITED KINGDOM.

The characterisation of interfaces at the atomic level provides useful experimental data for theoretical atomistic studies and materials problem solving. It is restricted to model structures that satisfy the requirements for experimental observations: edge-on boundaries and low index zone axes on either side. Happily, the improved resolution of modern microscopes helps to ease one restriction, allowing more closely packed structures and higher index zones. And advances in specimen preparation methods have increased the number of suitable boundaries. The deposition of gold onto (111) germanium substrates leads to the formation of mazed bicrystal films with faceted boundaries observable in plan view. Earlier work showed that for thicknesses of around 30nm, the boundaries of interest did not extend through the entire foil. This difficulty was solved by preparing a thinner film. High resolution images of the nominally 8nm thick film were recorded on the Stuttgart 1250kV ARM with the 0.144nm planes falling within the 0.12nm point-to-point resolution limit. The standard bicrystal misorientation, the 60 degree rotation about the film normal, predominates with {112} type facets. The problem of neighbouring facets causing different lattice displacements and what happens at a facet junction could now be properly investigated. The results were obtained with the help of image processing to analyse the geometric phase shifts across the boundary. Another bicrystal misorientation, a rotation of 19 degrees about the film normal, was observed for the first time. Most of the interfaces were inclined to the film normal (giving moire patterns and clues to the coincident site lattice) but some were edge-on. Preliminary results on a copper (111) bicrystal film will also be presented.

### Q9.6

FCC TITANIUM IN MULTILAYERS: A CAUTIONARY TALE. J.E. Bonevich and D. Josell, National Institute of Standards and Technology, Materials Science and Engineering Laboratory, Gaithersburg, MD.

When ultrathin layers of a material are deposited, the crystalline structure often differs from that predicted by the bulk equilibrium phase diagram. For example, Titanium (Ti) can deposit from the vapor with a face centered cubic (fcc) structure in films up to several monolayers thick, reverting to the bulk hexagonal close packed (hcp) structure in thicker layers. Reports in the literature have claimed the ability to fabricate stable multilayered structures of fcc-Ti and as well as hcp Aluminum (Al) in relatively thick multilayered films. A material with these novel structures might exhibit improved mechanical properties. We have investigated the important issue of fcc-Ti and hcp-Al formation in nanoscale multilayers by comprehensive comparison of x-ray diffraction (XRD) and transmission electron microscopy (TEM) results in these materials. Ti/Al multilayers with 7.2 and 5.2 nm composition modulation wavelengths were studied by reflection and transmission XRD as well as transmission electron diffraction (ED), high resolution TEM, energy-filtered imaging, and energy-dispersive spectroscopy. Our results demonstrate that the Ti and Al layers in these materials deposit in their bulk equilibrium forms and, further, that fcc-Ti can be obtained as an artifact of producing specimens for TEM. These results highlight the importance of coupling TEM techniques with XRD for detailed structural analysis of multilayer systems.

### Q9.7

MICROSTRUCTURAL CHARACTERIZATION OF METALS TREATED FOR HARDNESS AND CORROSION RESISTANCE WITH PULSED INTENSE ION BEAMS. T.J. Renk, P. Provencio, Sandia National Laboratories, Albuquerque, NM; and M.O. Thompson, Dept of Materials Science, Cornell University, Ithaca, NY.

Aluminum and titanium based alloys, with 0.1 - 4  $\mu\text{m}$  thick sputter-deposited transition metal coatings, were treated on the RHEPP-1 accelerator at Sandia National Laboratories using H, He, C, N, Ar, and Xe beams, with incident fluences up to  $10^9 \text{ J/cm}^2$  and cooling rates of  $10^8 - 10^9 \text{ K/sec}$ . This resulted in melt and resolidification of the surfaces. We investigated changes in the microstructure of treated samples that had improved performance in surface hardness and/or corrosion resistance. Using electron diffraction (SAD) and both bright field and dark field cross-sectional TEM (XTEM), we collected images from the surface regions to well into the depth of as-cast alloy. Compositional changes were measured by nanobeam energy dispersive spectroscopy (EDS). Treated samples show a consistent pattern of grain refinement with a somewhat coherent nano-scale microstructure of second-phase in the melted layer. EDS and XTEM observations of Pt-overcoated Ti-5 substrates are consistent with incorporation of Pt in solid solution at concentrations well above equilibrium values. These effects appear to be contributing to improved hardness. Further XTEM investigation

using dark field and bright field TEM and quantitative intensity measurements from digital images of thin regions show that dislocation density is very high below the melt zone and falls off gradually with depth indicating that ion beam effects occur well below the melt zone. The mixing of several transition metals into Al has also been examined to determine the origin of the improved corrosion resistance seen in those samples. XTEM shows that there is not coherent mixing of the melted layer, and no significant ion beam effects observed below the melt zone. \*This work was supported by the U. S. Department of Energy under Contract DE-AC04-94 AL85000. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy.

#### **Q9.8**

**EFTEM CHARACTERIZATION OF SEGREGATION IN CoCrPtTa/Cr MAGNETIC RECORDING MEDIA.** James E. Wittig, Vanderbilt University, Nashville, TN; James Bentley, Oak Ridge National Laboratory, Oak Ridge, TN; Thomas P. Nolan, Komag Inc., San Jose, CA.

Development of high-density longitudinal magnetic recording media with good noise performance and high thermal stability requires optimization of both alloy composition and processing methods. However, the nanoscale structural and chemical details that are needed for modeling and for guiding material development are not well understood. In CoCr(PtTa) thin film media, it is well established that intergranular Cr segregation is critical for good properties. We have used energy-filtered transmission electron microscopy (EFTEM) to characterize a series of CoCrTa/Cr, CoCrPt/Cr, and CoCrPtTa/Cr media sputtered under various processing conditions, in order to understand their structure-property-processing relationships. Elemental maps were produced by EFTEM methods that have been refined and optimized in a wide range of applications at the SHaRE facility over the last 4 years. Extraction of quantitative compositions at a spatial resolution approaching 1 nm involved treatments for diffraction contrast, variations in specimen thickness, and closely spaced ionization edges. Intergranular Cr segregation of  $\approx 4$ nm width is commonly observed. Compositions for hundreds of grain boundaries can be readily extracted from a single concentration map. Traditional AEM measurements are so tedious as to preclude such a statistically significant sampling. In addition, elemental maps are ideal for grain size measurements, since grains with sufficient intergranular segregation to be considered as isolated magnetic units are clearly defined. Elemental mapping of cross-sectioned specimens has revealed no enhanced intergranular segregation near the Cr underlayer; the segregation in the media is thus not due to grain boundary diffusion from the underlayer. The studies also indicate that even though the Ta is distributed uniformly, it may be more effective in promoting intergranular segregation than Pt. Research at the ORNL SHaRE User Facility was supported by the Division of Materials Sciences, U.S. Department of Energy under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corp., and through the SHaRE Program under contract DE-AC05-76OR00033 with Oak Ridge Associated Universities. Support from the Vanderbilt University Research Council and Komag Inc. is gratefully acknowledged.

#### **Q9.9**

**FORMATION OF AlN FILMS ON Ti/TiN ARC-LAYER INTERFACE WITH Al-0.5%Cu INTERCONNECTS EVALUATED BY XPS AND ENERGY FILTERED TEM.** J. Gazda, J. Zhao, P. Smith, A. White, Advanced Micro Devices, Process Characterization Analysis Laboratories, Austin, TX.

The use of Ti/TiN anti-reflective coatings (ARC) in photolithography of aluminum metal interconnect lines is widely used in the semiconductor industry. The quality and effectiveness of these coatings, however, depend strongly on the ability to control reaction products formed at film interfaces during processing. In the present study, formation of an Al-N compound at the interface between Ti/TiN ARC and Al-5%Cu interconnect was investigated. The effects of deposition temperatures for individual films and ensuing thermal cycling of the whole metal stack on intermetallic formation were evaluated. The composition and chemical bonding state of the aluminum nitride interfacial layer was evaluated by x-ray photoelectron spectroscopy (XPS) on blanket wafers. These results were combined with measurements made by energy filtered transmission electron microscopy (EFTEM) of thickness and continuity of the film. Energy filtered images were obtained with a Gatan imaging filter (GIF). Cross-sectional specimens were prepared by focused ion beam (FIB) for TEM studies. Formation of AlN or Al<sub>3</sub>N<sub>2</sub> was found to depend on the thermal cycling history of the metal stacks.

#### **Q9.10**

**EFFECTS OF DEPOSIT AND ALLOYING TEMPERATURE ON THE REDISTRIBUTION OF Cu IN 0.5% Cu - Al FILMS.** P.L. Smith

and J. Gazda, Advanced Micro Devices, Inc., Process Characterization Laboratory, Austin, TX.

Thermal distribution of Cu in Al-0.5% Cu metal interconnects were investigated using blanket and patterned films deposited on Si wafers. Copper elemental distributions were determined using Rutherford Backscattering Spectroscopy (RBS). Localized distributions of elemental Cu, Al<sub>2</sub>Cu and TiAl<sub>3</sub> precipitates within the Al grains were then evaluated by Energy Filtered Transmission Electron Microscopy (EFTEM) using a Gatan Imaging Filter (GIF). Both techniques showed that the formation or dissolution and subsequent redistribution of Cu within the metal stack were greatly influenced by deposition temperature, thermal history and the competitive formation of TiAl<sub>3</sub> intermetallics.

#### **Q9.11**

**ELECTRON ENERGY-LOSS NEAR-EDGE STRUCTURE OF SAPPHIRE.** Thomas Gemming, Stefan Nufer, Apostolos G. Marinopoulos, Sibylle Köstlmeier, and Christian Elsässer, Max-Planck-Institut für Metallforschung, Stuttgart, GERMANY.

Accurate measurements of electron energy-loss spectra of sapphire are especially important for an understanding of bonding at interfaces and grain boundaries. The specimen preparation influences the stability of a sapphire specimen under electron irradiation: For the same specimen it was found that an additional heat treatment step is very favorable concerning specimen stability, compared to a pure ion milling preparation using 6 kV argon ions. Additionally, the influence of the orientation of the sample was investigated with respect to the electron beam for bulk sapphire and for sapphire bicrystals. Orientations along and off specific zone axes were examined and also differences between low-index axes exhibiting mixed or pure arrangements of Al or O were studied. The experimental spectra were compared to results of density functional calculations. The measured ELNES intensity is assumed to be proportional to a projection of the calculated density of unoccupied states onto partial waves  $\varphi_{l,m}$  within a sphere around the scattering center. In analogy to optical spectroscopy the angular momentum  $l$  can be chosen according to the dipole selection rule. For the choice of  $m$  the direction of the incident electron beam plays an important role. We acknowledge the Volkswagenstiftung (Az I/70 502) for financial support.

#### **Q9.12**

**INTERFACIAL INTERACTION BETWEEN Cr THIN FILM AND OXIDE GLASS.** Nan Jiang, John Silcox, Cornell Univ, School of Applied and Engineering Physics, Ithaca, NY.

The interfacial interaction between Cr thin film and oxide glass has been observed by means of high spatial resolution electron energy loss spectroscopy. Knowledge of interface properties is important in understanding the mechanisms of adhesion of metal films to glasses, which have been receiving wide industrial uses, e.g. in flat panel displays. Generally, Cr provides good adhesion to most oxides due to the formation of the oxide layers. In this study, thin Cr films were evaporated in high vacuum on an alkaline earth aluminosilicate glass (Corning Code 1737) at room temperature. Using Cornell VG HB501 STEM, equipped with high energy resolved PEELS, the electronic structure can be probed to a sub-atomic level. Besides a partially oxidized Cr thin layer, a  $\sim 5$ nm wide Cr diffusion layer is seen. The electronic states of the Cr in this diffusion layer are different from that in the oxidized layer. The oxidation of Cr at the interface can result from the difference between the heats of oxide formation. In glass, bivalent ions randomly distribute in the SiO<sub>2</sub> network and bind weakly to non-bridging oxygen atoms. The oxidized Cr, Cr<sup>2+</sup>, may thus diffuse into glass, substitute the bivalent ions, and force them segregate to interface. Such exchanges, however, cannot continue forever. This is because the accumulation of alkaline earth elements at the interface can act as a diffusion barrier for Cr. Since Cr<sup>2+</sup> is not the most stable ionization state, the further interaction of Cr<sup>2+</sup> with Si<sup>4+</sup> in the glass network might occur. As a result, highly oxidized Cr states have been observed by EELS. Although there is no direct evidence to connect the diffusion layer with adhesion, it is quite plausible that the medium wide diffusion layer can provide better adhesion than those abrupt interfaces.

#### **Q9.13**

**FULLY QUANTITATIVE ANALYSIS OF INTERFACES IN CERAMIC MATERIALS BY SPATIALLY-RESOLVED EELS METHOD.** Hui Gu, JST Corporation, Ceramics Superplasticity Project, Nagoya, JAPAN.

With the high energy resolution of a FEG analytical electron microscope, spatial difference technique can be applied to the interface problems in various ceramic systems to the extent that, this practice becomes no longer subjective but instead, it provides indispensable and valuable quantitative information about the interface. All these are possible after comprehensively investigating the ELNES of the

relevant materials system as well as thoroughly evaluating the detector property. This can lead to reliable separation of interface signal from that (those) of the matrix. Several interfacial parameters, such as chemical composition, chemical width and elemental concentration can be obtained. Combined with the spectrum imaging technique, this can provide better performance as well as a measurable effective probe size. Examples are given from non-oxide structural ceramic systems like silicon nitride and carbides where a nanometer thick amorphous film is often found at grain boundary. However, this method is not limited to such cases; in the cases with special and other non-wetting boundary, the spectrum separation defines the grain boundary region on its own merit. Such definition is beneficial to overcome the uncertainty related to explanation of interfacial ELNES which are experiment dependent in many cases.

#### Q9.14

CHARACTERIZATION OF INTERGRANULAR PHASES IN DOPED ZIRCONIA POLYCRYSTALS. N.D. Evans<sup>1,2</sup>, P.H.

Imamura<sup>3</sup>, J. Bentley,<sup>2</sup> and M.L. Mecartney<sup>3</sup>; <sup>1</sup>Oak Ridge Institute for Science and Education, Oak Ridge, TN; <sup>2</sup>Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, TN; <sup>3</sup>Dept. of Biochemical Engineering and Materials Science, University of California, Irvine, CA.

In order to help make correlations between microstructure and prospects for superplastic forming, grain boundary chemistry in doped 3-mol%-yttria-stabilized tetragonal zirconia polycrystals (3Y-TZP) and doped 8-mol%-yttria-stabilized cubic zirconia (8Y-CSZ) specimens has been measured via high-spatial-resolution energy-dispersive X-ray spectrometry (EDS). Additives included glass (1 - 5 wt % silica, 1 wt % lithium-aluminum-silicate, 1 wt % barium-silicate, or 1 wt % borosilicate) or 10 wt % alumina. These constituents, which were added to accommodate strain and additionally impede grain growth in 8Y-CSZ, were chosen because they do not form intermediate phases during sintering or testing. Spectrometry was performed using an EMiSPEC Vision integrated acquisition system interfaced to a Philips CM200FEG AEM. EDS spectrum lines (typically 20 points, 0.5 to 2.0 nm spacing, 10 to 20 s dwell/point) were acquired across edge-on grain boundaries and across grain-boundary triple-points. The probe diameter was typically 2 nm (with ~1.5 nA), but to reduce beam damage noted in some specimens and to improve spatial resolution, some specimens were examined with a finer probe (1.2 nm FWHM; 0.5 nA). Some spectrum lines were acquired with automatic correction for drift. The results of this AEM study, and the correlations to observed mechanical properties germane to superplasticity (fracture characteristics and high temperature tensile deformation behavior), will be discussed.

#### Q9.15

MICROSTRUCTURE OF SrBi<sub>2</sub>Nb<sub>2</sub>O<sub>9</sub> AND SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub> EPITAXIAL THIN FILMS. Mark A. Zurbuchen, James Lettieri, Yunfa Jia, Altaf H. Carim, and Darrell G. Schlom, The Pennsylvania State University, Dept of Materials Science, University Park, PA; Wei Tian and Xiaoqing Pan, The University of Michigan, Dept of Materials Science and Engineering, Ann Arbor, MI.

SrBi<sub>2</sub>Nb<sub>2</sub>O<sub>9</sub> and SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub> thin films were grown by pulsed laser deposition (PLD) on (110) NdGaO<sub>3</sub> and on (100) and (110) SrTiO<sub>3</sub>. The films were examined by high-resolution transmission electron microscopy (HRTEM) to determine the interface and defect structure. (001) oriented films were grown on (110) NdGaO<sub>3</sub> and (100) SrTiO<sub>3</sub>. These *c*-axis oriented films consisted of many identically-oriented epitaxial domains offset by some fraction of the unit cell *c*-dimension, resulting in meandering out-of-phase boundaries (OPBs) between domains. Causes of the misregistry of neighboring nuclei were investigated. Clean film/substrate interfaces were imaged, and the atomic structure at the interfaces was determined by comparison of HRTEM simulations of models to actual images. An intermittent epitaxial interfacial phase ( $\approx 150$  Å thick) was observed in some samples, and was determined to be  $\beta$ -Bi<sub>2</sub>O<sub>3</sub>. Subsequent adjustment of the deposition parameters yielded films free of this interfacial layer. On (110) SrTiO<sub>3</sub> substrates, an epitaxial SrRuO<sub>3</sub> electrode was grown prior to deposition of the SrBi<sub>2</sub>Nb<sub>2</sub>O<sub>9</sub>. The SrRuO<sub>3</sub>/SrBi<sub>2</sub>Nb<sub>2</sub>O<sub>9</sub> interface is rough ( $\pm \approx 150$  Å), but free of impurity phases. SrBi<sub>2</sub>Nb<sub>2</sub>O<sub>9</sub> grows epitaxially on (110) SrTiO<sub>3</sub> and (110) SrRuO<sub>3</sub>/SrTiO<sub>3</sub>, with the (001) plane of the SrBi<sub>2</sub>Nb<sub>2</sub>O<sub>9</sub> parallel to the (100) planes of the substrate. Two of the three degenerate ways in which this epitaxial orientation can occur were observed to dominate, and the microstructure of SrBi<sub>2</sub>Nb<sub>2</sub>O<sub>9</sub> boundaries between these two orientation variants was studied.

#### Q9.16

Mg(OH)<sub>2</sub> DEHYDROXYLATION: A LAMELLAR NUCLEATION AND GROWTH PROCESS. Michael J. McKelvey<sup>a,b</sup>, Renu Sharma<sup>a,b</sup>, Andrew V.G. Chizmeshya<sup>a</sup>, Ray W. Carpenter<sup>a,b</sup> and Ken Streib<sup>b</sup>, <sup>a</sup>Center for Solid State Science, Arizona State University, Tempe, AZ;

<sup>b</sup>Science and Engineering of Materials Ph.D. Program, Arizona State University, Tempe, AZ.

Fossil fuels, especially coal, can support the energy demands of the world for centuries to come, if the environmental problems associated with CO<sub>2</sub> emissions can be overcome. Permanent and safe methods for CO<sub>2</sub> capture and disposal/storage need to be developed. Mineralization of stationary-source CO<sub>2</sub> emissions as carbonates can provide such safe capture and long-term sequestration. Mg(OH)<sub>2</sub> carbonation is a leading process candidate, which generates the stable naturally occurring mineral magnesite (MgCO<sub>3</sub>) and water. Key to process cost and viability are the carbonation reaction rate and degree of completion. This process, which involves simultaneous dehydroxylation and carbonation is very promising, but far from optimized. Since Mg(OH)<sub>2</sub> dehydroxylation is intimately associated with the carbonation process, its mechanisms are of direct interest in understanding and optimizing the process. Although Mg(OH)<sub>2</sub> dehydroxylation has been extensively studied, relatively little is known about the atomic-level nature of the process, especially in the early stages. Herein, we report on our investigation of the dehydroxylation process using environmental-cell, dynamic high-resolution transmission electron microscopy to directly observe the process at the atomic-level for the first time. These observations are combined with advanced computational modeling studies using a non-empirical density functional theory approach to better elucidate the atomic-level process. Dehydroxylation follows a lamellar nucleation and growth process involving oxide layer formation. These layers form lamellar oxyhydroxide regions, which can grow both parallel and perpendicular to the Mg(OH)<sub>2</sub> lamella. The number of oxide layers within the regions increases as they grow during dehydroxylation. Selected area diffraction suggests a novel two-dimensional variant of Vegard's law can describe the oxyhydroxide regions, with intralamellar Mg-Mg packing distances observed between those known for Mg(OH)<sub>2</sub> and MgO. Intralamellar and interlamellar elastic stress induced during dehydroxylation can contribute to crystallite cracking and MgO surface reconstruction.

#### Q9.17

THE EFFECT OF DIFFERENT OXIDIZING ATMOSPHERES ON THE INITIAL KINETICS OF COPPER OXIDATION AS STUDIED BY IN SITU UHV-TEM. Mridula Dixit Bharadwaj, Anu Gupta, Judith Yang, Univ. of Pittsburgh, Dept of Materials Sci. & Eng., Pittsburgh, PA.

A crucial area where nucleation and growth processes are not yet well understood is metal oxidation. Copper has played a significant role in the development of oxidation theories, ranging from the classic oxidation studies on the epitaxial growth of the thermodynamically stable oxide scale to the surface science investigations of the dynamics of oxygen interaction with the bare metal surface. To gain further fundamental and unique insights into the nucleation and initial growth of the metal oxide, we are visualizing the initial oxidation stage of copper by in situ ultra-high vacuum (UHV) transmission electron microscopy (TEM). The oxidation reactions for metallic systems is extremely sensitive to the oxidizing environment. Steam or hydrogen within the oxide scale is known to prevent loss of contact between the scale and the metal. We have shown previously that oxygen surface diffusion is the dominant mechanism for the initial oxide formation for oxidation in dry oxygen. We will now focus on the role moisture plays in the solid state reactions involved in copper oxidation. Our initial observations show that water vapor reduces the oxide as well as reduce the rate of oxidation if both O<sub>2</sub> and H<sub>2</sub>O are used. Quantification of these data should provide key insights into the structural effects of moisture on the initial kinetics of the oxidation reaction.

#### SESSION Q10: INTERFACES IN METALS AND CERAMICS II

Chairs: Uli Dahmen and Joachim Mayer  
Friday Morning, December 3, 1999  
Salon A/B (M)

#### 8:30 AM \*Q10.1

THE ROLE OF MICROSCOPY IN STUDIES OF CURRENT TRANSPORT ACROSS GRAIN BOUNDARIES IN HIGH TEMPERATURE SUPERCONDUCTORS. Dean J. Miller, Materials Science Division, Argonne National Laboratory, Argonne, IL.

The mechanisms of current transport and dissipation across grain boundaries in high temperature superconductors remains one of the more compelling topics of the field. The study of these issues has required contributions from a variety of techniques and disciplines, including various microscopies. In this work, the important role microscopy has played in understanding the influence of the grain boundary structure on properties will be emphasized. This work is characterized by the broad array of techniques required to carry out

the most insightful experiments. For example, TEM is used extensively to characterize the local physical and chemical structure of the boundaries while SEM and EBSP are used to probe the global structure and to map the misorientation across various boundaries. Polarized light microscopy plays an important role as well, not only in the characterization of boundaries but as a tool in isolating segments of individual boundaries for the measurement of properties. The essential role that each of these techniques plays in developing a better understanding dissipation across grain boundaries in high temperature superconductors will be presented and discussed.

#### 9:00 AM \*Q10.2

INVESTIGATING THE ATOMIC SCALE STRUCTURE-PROPERTY RELATIONSHIPS AT GRAIN BOUNDARIES IN OXIDE MATERIALS. Nigel D. Browning, Susanne Stemmer, Edward M. James, James P. Buban, Kyosuke Kishida, Julie A. Zaborac, University of Illinois at Chicago, Department of Physics, Chicago, IL; Gerd Duscher, Vanderbilt University, Department of Physics, Nashville, TN; Miyoung Kim, Stephen J. Pennycook, Oak Ridge National Laboratory, Solid State Division, Oak Ridge, TN.

Grain boundaries are known to dominate the electronic properties of a wide range of oxide materials. To understand the properties of these boundaries, it is typically assumed that they act as a perfect source/sink for vacancies, and that the difference in formation energies for anion and cation vacancies leads to a charged grain boundary plane and an adjacent compensating space-charge region. The formation of this back-to-back Schottky barrier potential at the boundary generally produces models that are in agreement with the observed electronic properties. However, there are technologically relevant cases when this analysis breaks down and the electronic properties of the boundaries appear to be in violation of this simple picture. The combination of Z-contrast imaging and electron energy loss spectroscopy (EELS) in the scanning transmission electron microscope (STEM) provides an ideal experimental means to investigate the structure-property relationships at grain boundaries in oxide materials. Both techniques can be performed at the same time with atomic spatial resolution, allowing a direct correlation between the atomic structure, composition and local electronic structure at defined locations within and around the boundary. These experimental techniques have been used to characterize grain boundaries in a variety of oxide systems with the same perovskite crystal structure. Although the materials themselves have widely varying compositions and are being developed to take advantage of different electronic properties, we find that SrTiO<sub>3</sub>, Sr(Ti,Mn)O<sub>3</sub>, (Ba,Sr)TiO<sub>3</sub>, YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-d</sub>, (Bi,Pb)<sub>2</sub>Sr<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>8</sub> all exhibit the same structural, compositional and electronic structure features at their grain boundaries. These features can be related to the well known chemistry of the perovskite family of compounds, and the modifying effect of the grain boundary structure on the thermodynamic model for vacancy formation can be determined.

#### 9:30 AM \*Q10.3

DYNAMICS OF NANOSCALE PHENOMENA VIA IN-SITU TEM. Kevin D. Johnson, Xiwei Lin and Vinayak P. Dravid, Department of Materials Science & Engineering, Northwestern University, Evanston, IL.

A large number of functional electronic devices are operative under the influence of an external electrical field/current. It is under such applied electrical stimulus, the various dynamic properties of electrically active interfaces emerge: e.g. C-V, I-V, P-E curves. It is of great interest to monitor the functional processes in dielectric and ferroelectric devices, directly - in real-time and real-space, via high spatial resolution and analytical techniques. We have developed several in-situ TEM tools and techniques to probe various aspects of electrically active interfacial systems under the influence of applied electrical field/current. Two examples of dynamic experiments via in-situ TEM will be presented. In first, our interest is in the behavior of ferro-/piezoelectric domains and their interactions with the microstructure in PZT/PMN-PT films. In the second case, we monitor the behavior of space-charge potential (Schottky barrier) across grain boundaries and film-electrode interfaces using in-situ electron holography. In both cases, microlithography techniques have been employed to pattern 'TEM-ready' specimens to ensure that the bulk electrical behavior is maintained in TEM thin foils. Such experiments have provided unique insights into the genesis of domain switching, barrier breakdown and their connection to microstructure and microchemistry of various interfaces involved in the device performance.

#### 10:30 AM \*Q10.4

APPLICATION OF ELECTRON MICROSCOPY TO THE DESIGN OF HARD COATINGS. Lars Hultman, Thin Film Physics Division, Department of Physics, Linköping University, SWEDEN.

The design of advanced hard coating materials requires understanding

and control of chemical bonding and microstructure. Coatings of interest include ceramics often under a high compressive residual stress state from quenched point defects as the result of the ion-assisted deposition method employed, metastable alloys, nanostructured composite materials, nanolaminated heterostructures (superlattices), and amorphous-to-fullerene-like carbon nitride films. This presentation will discuss the application of electron microscopy techniques for some thin film synthesis topics of importance. Diamond-like carbon and carbon nitride coatings often display an inhomogeneous microstructure, e.g., diamond precipitation and nanotubular or fullerene-like domains. Here, sub-nm-scale EELS chemical mapping and fine-structure analysis of elemental K-edge absorption edges will be reviewed. Results show that N is doped homogeneously into a network of curved and interlinked graphitic basal planes. For C-B-N nanoboxes grown in a solid matrix by reactive magnetron sputtering at low-T (350 C), an immiscibility between BN and C(N) was established. Also, C-N and B-C bonding was observed for these structures in addition to the commonly observed B-N and C-C. Thus, the magnetron discharge conditions is a promising approach for controlling the chemical composition of nanostructures in the B-N-C ternary system. Film growth under low-energy ion bombardment - typical condition for physical vapor deposition methods employed for hard coatings - gives rise to residual point defects. Examples will be given from the analysis of dislocation loops, voids, and gas bubble precipitation in TiN. Superlattice structures can exhibit coherency strain or relaxation by misfit dislocations at interfaces. Examples are given from two systems; TiN/NbN (exhibiting non-linear interdiffusion) and Y<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> (including the formation of a defect fluorite structure). Here, HREM image processing including displacement field analysis will be reported. Finally, present models for superhardening in nanolaminates rest on the premises of dislocation hindering at interfaces. Results will be presented for the mechanically induced deformation zone in TiN/NbN which shows glide limited to within layers of the superlattice.

#### 11:00 AM Q10.5

INTERFACE ENGINEERING IN A COMBINED ARC/ UNBALANCED MAGNETRON DEPOSITION SYSTEM DURING GROWTH OF Ti<sub>0.5</sub>Al<sub>0.5</sub>N FILMS ON STEEL: AN XTEM STUDY. I. Petrov, R.D. Twisten, Fredrick Seitz Materials Research Laboratory, University of Illinois, Urbana, IL; C. Schoenjahn, L.A. Donohue, D.B. Lewis, W.D. Muenz, Materials Research Institute, Sheffield Hallam University, UNITED KINGDOM.

XTEM studies of interfaces formed during PVD growth of transition metal nitrides on steel have provided crucial information for the development of novel techniques of interface engineering. In-situ substrate cleaning by ion etching prior to deposition is a key step in achieving good film adhesion, which is essential for all coating applications. Irradiation with metal or gas ions alters substrate surface chemistry, topography and microstructure thus affecting subsequent film growth. This study compares Ti<sub>0.5</sub>Al<sub>0.5</sub>N/ steel interfaces formed after Cr- metal ion bombardment at negative substrate biases, U<sub>s</sub>, ranging from 600 to 1200 V during a Cr cathodic arc, stabilized with a 0.06 Pa Ar background pressure. Samples pretreated with a 1200 V Ar glow discharge at a pressure of 0.6 Pa were also investigated. Microstructure and microchemistry of the interfaces was studied by XTEM samples using STEM-EDX analysis. Cr ion etching with U<sub>s</sub> = 1200 V resulted in a net removal of over 100 nm of substrate material with the formation, through implantation and radiation-enhanced diffusion, of a Cr-enriched near-surface region extending to a depth of -10 nm. As U<sub>s</sub> was reduced to 600 V, Cr accumulated at the surface as an 5 nm thick layer. Ar was incorporated at the surface to levels of 4 and 5 at% during Cr arc-etching and Ar glow discharge, respectively. Microstructure of Ti<sub>0.5</sub>Al<sub>0.5</sub>N overlayers was dramatically affected by pre-treatment procedures. Ar sputter cleaned steel surfaces (U<sub>s</sub> = 1200 V) promote nucleation of randomly oriented grains leading to a competitive column growth with small column size and open boundaries. In contrast, Cr irradiation at the same bias voltage results in local epitaxial growth of Ti<sub>0.5</sub>Al<sub>0.5</sub>N on steel, which is expected to improve film/substrate adhesion. Coatings deposited after Cr treatment with U<sub>s</sub> = 600V still exhibit small areas of oriented growth but porosity is also present.

#### 11:15 AM Q10.6

ATOMIC SCALE ANALYSIS AND MODELING OF CUBIC ZIRCONIA GRAIN BOUNDARIES. Elizabeth Dickey, Susan Sinnott, Xudong Fan, Ma Yong, Department of Chemical and Materials Engineering, University of Kentucky, Lexington, KY.

Coupling high-resolution microscopy with atomistic simulations is an extremely powerful approach to understanding grain boundary and interfacial phenomena in materials. Here we present complementary experimental and theoretical analyses of grain boundaries in yttria-stabilized cubic zirconia. Z-contrast scanning transmission electron microscopy and electron energy loss spectroscopy (EELS) are employed to study the structure and chemistry of 24 and 36.8 degree

symmetric tilt [100] grain boundaries. Periodic structural units are defined for both boundary configurations from the Z-contrast images. Partially occupied Zr columns in the grain boundary core are observed which allow the Zr atoms to stagger along the beam direction and thus avoid cation crowding. Column by column EELS indicates changes in cation coordination in the boundary core. Using the experimentally-derived structural models as input models, ab-initio calculations using density functional theory are performed. The structures of the grain boundaries are refined and local coordination and electronic structures are calculated. The role of partial column occupancy in grain boundary relaxation will be discussed in light of the theoretical calculations. Agreement between experiment and calculations will be discussed.

#### 11:30 AM Q10.7

**REAL TIME OBSERVATION OF GRAIN GROWTH IN SPUTTERED Ag AND TiO<sub>x</sub> THIN FILMS.** R. Dannenberg, BOC Coating Technology, Fairfield, CA; E.A. Stach, National Center for Electron Microscopy, Lawrence Berkeley National Laboratory, Berkeley, CA; J.R. Groza and B.J. Dresser, Department of Chemical Engineering and Materials Science, University of California at Davis, CA.

In-situ annealing in the transmission electron microscope allows for real time observation of grain growth and crystallization phenomenon in thin films. In this work, silver films are DC sputter deposited onto commercially available silicon nitride window TEM membranes, and then annealed in the microscope for various temperatures and hold times. The grain size distribution of the as-deposited films is bimodal, with large abnormal grains of approximately 100 nm in diameter, embedded in a matrix of smaller grains of 15 nm diameters. Coarsening begins at temperatures of approximately 100°C, and quickly reaches a plateau. The grain growth process restarts only after sufficient temperature increases, and plateaus at each succeeding temperature. Using a variation of the Mullins - Von Neumann law, the activation energy for the abnormal growth is found to be 0.23 eV, consistent with previous reports for surface diffusion. Grain growth appears to stop above temperatures of 350°C, eventually leading to triple junction pore formation at 350°C and de-wetting of the film from the substrate at 600°C. The de-wetting failure is the high temperature limit of the thermal grooving that acts to cancel the driving force for grain growth at the lower temperatures. Real time TEM images as evidence of this effect are presented, along with observations of pore formation that support surface diffusion as the mass transport mechanism. Additional studies of the crystallization of reactively sputter deposited amorphous TiO<sub>x</sub> films are presented, and compared directly to Monte Carlo simulations of the Kolmogorov-Johnson-Mehl-Avrami (KJMA) crystallization equation. Measurement of grain distributions and boundary velocities act as input to the KJMA simulations, and are used to infer numerical values for growth kinetics. These results demonstrate the utility of in-situ annealing within the TEM for quantitative determination of grain growth kinetics.

#### 11:45 AM Q10.8

**CHARACTERIZATION OF A METAL-CERAMIC BRAZE BY SEM-EDX SPECTRUM-IMAGING AND MULTIVARIATE STATISTICAL ANALYSIS.** Paul G. Kotula, J.J. Stephens, Sandia National Laboratories, Albuquerque, NM; Ian M. Anderson, Oak Ridge National Laboratory, Oak Ridge, TN.

EDX spectrum-imaging, where a full energy-dispersive X-ray (EDX) spectrum is acquired for each pixel in a two-dimensional array, has been combined with multivariate statistical analysis (MSA) to characterize the significant microchemical features of a metal-ceramic braze microstructure in the scanning electron microscope (SEM). The braze has a sandwich geometry, with two pieces of alumina, two braze layers and a Kovar alloy filler material (principally iron, nickel and cobalt). The braze layers are composed of a copper-silver eutectic containing some titanium, which is incorporated to promote chemical bonding at the alumina-braze interface. A 100 x 75 pixel spectrum-image was acquired from the alumina-braze interface region with 200 nm pixel spacing and 10 kV operating voltage. Conventional X-ray maps show that the titanium is indeed distributed along the interface, as a narrow reaction layer punctuated by hemispherical pockets that protrude into the braze layer. MSA of the spectrum-image identifies six distinct phases in the analyzed volume, including major phases corresponding to distinct silver and copper solid solutions in the eutectic braze layer, and the alumina grains and glass sintering aid in the alumina ceramic. Significantly, MSA identifies the thin reaction layer and hemispherical pockets as being two distinct phases in the titanium-enriched region at the interface, the latter phase containing significant amounts of iron, nickel and cobalt from the Kovar alloy. This distinction could be revealed by mapping of the iron, nickel or cobalt, but such maps may not have been formed since these elements have dilute concentrations in the microstructure as a whole. The partitioning of titanium between the two phases may affect the degree of chemical bonding at the interface.