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
Chair: Matthew R. Liber and Ivan Petrov
Tuesday Afternoon, November 30, 1999
Salon A/B [M]

12:30 PM *Q1.1
MAGNETISM, MICROSTRUCTURE AND MATERIALS CHARACTERIZATION WITH ELECTRON PROBES: ADVANCES AND APPLICATIONS
Ruslan M. Khasanov, Ed. Girt, G. Kissin and H. J.having, Materials Department, National Center for Electron Microscopy, Lawrence Berkeley National Laboratory, University of California, Berkeley, CA.

The key parameters defining the magnetic behavior of materials are coercivity, remanence, permeability and hysteresis loss. These characteristics can be controlled by the microstructure of the material and magnetic domains. The magnetic properties of thin films and nanostructures, which are not accessible to the novel physical properties observed, such as perpendicular anisotropy. The magnetic properties are due to the physical and chemical structure of the interfaces. In nanostructured materials, the coercivity and remanence can be controlled by controlling grain size, shape, defects, and most importantly, the intergranular coupling and/or isolation. Previous breakthroughs in magnetic materials follow from both advances in material synthesis and the ability to characterize them by advanced electron-optical methods at the nanometer length scale. Research in these areas will be described, drawing on recent examples, to illustrate the relationship between magnetic properties and advanced TEM characterization methods. In particular, some examples will include: (a) magnetic nanostructures and inter-granular coupling in metallic nanostructures; (b) inter-granular coupling in hard magnetic thin films and nanostructures; and (c) unusual substitution effects and description of the conductivity mechanisms associated with the magnetic nanostructures.

2:00 PM *Q1.2
ELECTRON HOLOGRAPHY OF NONSTRAUTED MAGNETIC MATERIALS
R.E. Binnig, R. Kowalski, and J. Kowalski, Center for Solid State Science, Arizona State University, Tempe, AZ.

Electron holography provides a unique method for probing the magnetization behavior of materials. In this study, the magnetization behavior of nonstructured magnetic thin films has been investigated using electron holography and the results have been compared with magnetization measurements. Initial studies focused on rectangular Co elements, with magnetic fields applied to the sample in situ. Order parameters for the elements were determined. Further observations involved a magnetized sample resembling a magnetic layer, with numerous regions placed on the surface, and on the surface, the remaining regions involved a magnetic layer resembling a magnetic layer. The observations showed that the magnetic behavior of the magnetic elements is determined by the interaction between the elements, but they do not fully explain the measured magnetic 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 magnetic characterization is important to understanding the magnetic performance of thin films, due to the magnetic properties. With cobalt alloy grain sizes typically in the range 15-20 nm, high-resolution imaging is essential. The grain size distribution quantitatively in as function of deposition conditions. Grain size segregation is an important parameter determining magnetic properties, which can be studied both by energy dispersive spectroscopy and by energy filtering imaging techniques. To correlate this information with the magnetic structure, Lorenz imaging methods are employed. The biaxial transition regions can be correlated with the magnetic structure, and the results show that the demagnetized Lorentz structure depends strongly on the degree of magnetic coupling 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 Ni-Fe-B MAGNETS
Yael V. Volkov 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 NiFe-B magnets prepared by different processing methods. The magnetic TEM observations in Fresnel imaging have been carried out using JEOL 2000FX and JOEL3000FXE microscopes under the fine-focus control mode with an objective lens. The field of view over which the magnetic images were recorded is approximately 100 x 100 nm. The results of the experiments were recorded on videotapes. The advantages of the field emission gun (FEG) over the LaB6 method allowed us to realize a novel phase-coherent 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 imaging techniques have been successfully used to characterize the magnetic behavior of GBs in NiFe-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 magneto-static charges and/or dipoles. They also serve for smooth transition of 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 video presentations.

3:30 PM *Q1.5
BEYOND LEEM: SPELEM AND SPELEEM
K. H. Buhner, Thomas Schmidt, ELETTRA, Trieste, Italy.

LEEM is an imaging technique with slow electrons which gives information about the surface structure and composition. In this work, we have extended the low energy electron microscopy (LEEM) to optical imaging by combining LEEM with spectroscopic photoemission microscopy (SPIEM) and to chemical and electronic imaging by combining LEEM with secondary electron imaging. As a result, comprehensive surface analysis with high sensitivity to surface electronic structures, chemical composition, and electronic structure is possible. In this talk, I will present recent results related to the growth of thin films and nanostructures, including SiOx and Si, as well as semiconductor films on Si substrates.

4:00 PM *Q1.6
LOW ENERGY ELECTRON MICROSCOPY
T.J. Watson, Department of Physics, University of Wisconsin, Madison, WI.

LEEM is one of the few electron microscopy methods that allow observation of a specimen surface microscope to observe the surface of crystalline thin films. Low-energy electron microscopy (LEEM) is useful for studying the surface of thin films and nanostructures, including SiOx and Si, as well as semiconductor films on Si substrates. However, LEEM is not suitable for studying the surface of thin films and nanostructures with high sensitivity to surface electronic structures, chemical composition, and electronic structure.

4:30 PM *Q1.7
LEEM STUDIES OF BCC REFRACTORY METAL HETEROEPITAXY: C.F. Flynn and W. Schiewe, University of Illinois at Urbana-Champaign, Materials Research Laboratory, Urbana, IL.

We have devised methods that permit LEEM investigations of a single crystal films grown on conducting or insulating substrates, and at low temperatures. Here we describe studies of Ni (110) and Nb (110) grown 50-100 nm thick by molecular beam epitaxy on sapphire (1120). By Low Energy Electron Microscopy (LEEM) we can observe the evolution of structural features at the interface, in the bulk and at the outer surface. In this contribution, four critical aspects of the thin film evolution are discussed: (1) The phases 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 small surface step bunching occurs. (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 low-symmetry or low-energy orientations, including slip from interfacial dislocations of various observed types and orientations. (4) Complex and newly observed interactions among these three categories of processes, of which illustrative examples are (a) the way surface recombinations intersect 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
Chair: James Bentley and Kristin M. Krishnan
Wednesday, December 1, 1999
Salon A/B (M)

8:30 AM Q2.1

Electron backscatter diffraction (EBSD) has become a standard tool for the microstructural characterization of crystalline materials. One of the big advantages of EBSD over other characterization methods has been the lack of a robust way to obtain crystallographic information about the specimen. The advent of EBSD has overcome this disadvantage. The initial use of EBSD 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 microstructural nucleation sites and to make phase maps 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 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 that are then used along with the sample chemistry to search a database 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 advancements in the understanding of the information content of EBSD patterns may enable the Beynon lattice to be calculated directly from the pattern.

9:00 AM Q2.2
RECONSTRUCTION OF A 3D MICROSTRUCTURE USING ORIENTATION IMAGING MICROSCOPY: Wayne E. King, James S. Stoklen, Adam J. Schwartz, Mark A. Wall and Lon Nguyen, Lawrence Livermore National 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 orientation and grain topology of bulk single-crystal Ta. The average grain size of the material was 4×10 μm². OIM scans encompassed regions of dimension 1200×1200 μm² sampled over a hexagonal grid with 4.5 μm spacing. Data from forty-seven serial sections separated by 4.9 μm (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 computed 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 calculated. 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 CUBED HOLZ PATTERNS: Junya Inoue, Department of Civil Engineering, University of Tokyo, Tokyo, JAPAN; Alan F. Scherer, Lumber 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 LaB₆ microscope. This technique allows determination of the full strain tensor within ±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 the experimentally determined projector lens distortion. Concurrently, for small uniform strains, theoretical simulations are performed to derive an x-y Thinning design function that 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 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 mixed bicrystalline microstructure.

9:30 AM Q2.4
STUDIES OF GAS-SOLID INTERACTIONS IN A TRANSMISSION ELECTRON MICROSCOPE: L.M. Robertson, Dept of Material Science and Engineering, Urbana, IL.

A differentially pumped, double-aperture limited environmental cell has been installed in the objective polepiece 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 streaming stages with temperature control from 100 to 1200°C 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 characterizing the nanoscale, many-body atomic ordering effects on the properties of ordered aluminide intermetallic alloys. Whereas early formulations of ALCHEMI yielded inaccurate and sometimes unphysical atomic site distributions for aluminide 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 ion beam delocalization and material drift, and will address these factors are addressed in recent formulations of the technique. The results of extensive ALCHEMI measurements on B3-ordered aluminide 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 predict the 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-AC05-84OR21400 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 behavior of materials. To study property-determining valence-electrons distribution in semiconductors, we developed a novel technique via Parallel Recording Of Diffraction Intensity (PARODI) as a function of
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 A MORPHOUS SEMICONDUCTORS REVEALED BY FLUCTUATION MICROSCOPY

Fluctuation microscopy is a new technique for gaining 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 diffraction 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 1.5 nm, which has lead us to the development of a model for their structure [M. J. Treaty, J. M. Gibson, and P. J. Keblishki, 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. Lithography produces a smooth, atomically flat surface, the effects of which have implications for the SbSb-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 SINGLE-CRYSTAL HETEROSTRUCTURES
Brian Forest, 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 mismatch dislocations. The energetic and kinetic generation of mismatch 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 mismatch dislocation array. Experimental results have been obtained for the Ge/Si, Ge/SiGe, InGaAs/InP 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 carriers 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. Benn, J. Demarest, D. Dunn, W. M. Bothe and Q. Yuan (U. Virginia), E. Stein (LBL) and M. T. 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 3D-2D epitaxy, with the intriguing prospect of band-gap engineering in a lattice-matched system; b) CdTe/Se 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/AlGaN/InGaN/GaN 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. Electro-optic holography enables to extract composition profiles and electric fields across GaN/AlGaN/InGaN and GaN/InGaN/GaN quantum wells. In addition, electron holograms recorded on the [110] zone-axes of GaN/AlGaN/InGaN/GaN quantum 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 holographs on the zone-axes. We have tilted the GaN/AlGaN/InGaN/GaN samples away from the zone-axes to minimize the dynamical scattering effect. A phase shift of $\pm 2\pi$ rad across the GaN/AlGaN/InGaN/GaN quantum well was observed on a nanometer scale before and after tilting away from the zone-axes. This observed phase shift across GaN/AlGaN/InGaN/GaN 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 Ratier, Gerard Novot, Laboratoire d'Etudes et de Recherches sur les Matériaux, UPRERA CNRS 5120, EMIRA, Caen, FRANCE; Philippe Vermaut, Laboratoire de Métallographie Structurale, Ecole Superieure de Chimie de Paris, Paris, FRANCE; Abdel Redjoumi, Laboratoire de Science et Genie des Surfaces, CNRS, Ecole des Mines, Nancy, FRANCE; Jean-Paul Mermohli, EUBD, Villeuneuve d'Ascq, FRANCE; Ann Vila, Departement d'Electronique, Université de Barcelona, Barcelona, SPAIN; Marc Lebradour and Roland Bonnet, Institut National Polytechnique de Grenoble, UTPCM, St-Martin d'Heres, 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 was envisaged. The use of three methods at least in order to completely solve the problem. In this contribution it will be shown that the combination method which uses a very small diameter parallel beam allows to completely solve the complete local symmetry and the case study will be presented in an austenitic 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 polyn 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 combination 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. It is also possible to combine structuring 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 prism faults in GaN thin films.

3:45 PM Q3.6
STEM BASED MEASUREMENTS OF LATERAL COMPOSITION MODULATION IN InAlAs FILMS, R. W. Martin, University of Illinois, Urbana, IL; D. M. Folkerts, J. L. Reno, Sandia National Laboratories, Albuquerque, NM; J. Mirecki Millham, University of Michigan, Ann Arbor, MI; A. G. Norman, S.P. Ahrentzel, A. Maciejewski, 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 (SPL) of III/V materials. We have analyzed films consisting of InAlAs/AlGaAs SPL which exhibit a 2D square lattice (~4 monolayers) grown on InP substrates under a range of conditions.

Electron microscopy 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 (~0.4%) with respect to the InP, EDS analysis reveals an InAs enrichment of 0.23 mole fraction but only 0.15 In mole fraction depletion in the regions. HAADF imaging reveals this is the result of an asymmetric modulation profile consisting of sharply peaked InAs rich regions (~4nm wide) separated by broad regions of AlAs rich material (~10nm wide). This degree of In enrichment is consistent with the red shift observed in our photoluminescence measurement. HAADF imaging also reveals presence of interlayer mixing of the SPL 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-FG02-89ER45439. The authors acknowledge the support of the U.S. DOE, OER/ES Division of Materials Science grant DE-AC02-83CH00016, and support for Sandia National Laboratories by the U.S. DOE contract DE-AC04-94AL85000.

4:00 PM Q3.7
ENERGY-LOST FILTERED IMAGING OF SEGREGATION, INDUCED INTERFACE BROADENING IN SiGe/Si p-CHANNEL MOSFET DEVICE STRUCTURES, D. L. Norris, A. G. Cullis, Dept. of Electronic and Electrical Engineering, University of Sheffield, SHEFFIELD, UNITED KINGDOM; T. J. Green, 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 mobility compared with conventional silicon based devices. This derives, in particular, from the modification of the band structure owing to pseudomorphic strain of the alloy channel; however, the approach relies heavily on producing uniform SiGe layers with highly abrupt interfaces. Hence the dependence of hole mobility on interface sharpness is not easy to control and, therefore, it is crucial to analyse the SiGe channel on a nanoscale to determine the finest details of composition gradations. Chemical profiles across such layers obtained from conventional 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 nanoscale by using advanced energy-loss filtering in the field emission gun TEM to enhance electron energy-loss spectroscopy and Electrons image phase images have been employed. In this paper, we will show that the distribution of Ge across the channel interfaces is asymmetric due to the effects of segregation during growth. A quantitative comparison will be made between these composition measurements, concerning similar studies of similar samples, and the predictions of theoretical models of the segregation phenomenon.

4:15 PM Q3.8

We report measurements of the distribution of Sn atoms in 3-doped Si, on a nanoscale. Both 2-D and 3-D concentration maps were obtained using electron energy loss spectroscopy and electron energy loss imaging. Both techniques are sensitive to locate Sn 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, Y-W. Bialaczo, K. Siegrist, R.J. Planoef, E.D. Williams, University of Maryland, Dept. of Physics, College Park, MD.

One of several possible contrast mechanisms in Photoelectron Emission Microscopy (PEEM) is that of photoemission from band edges [1]. In silicon, the effective photothreshold can be reduced by degenerate
4:45 PM Q5.10 IN SITU ANNEALING TRANSMISSION ELECTRON MICROSCOPY (TEM) STUDY OF THE Pd/Ge/Pd/GaAs INTERFACIAL REACTIONS. P. Radlakus, J. M. McCarthy, Oregon Graduate Institute of Science and Technology, Dept. of Materials Science and Engineering, Portland, OR; E. A. Sirch, Lawrence Berkeley National Laboratory, National Center for Electron Microscopy, Berkeley, CA.

In situ TEM annealing experiments on the Pd (20 nm)/Ge (150 nm)/Pd (50 nm) system have proven 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 in temperatures between 1300°C and 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 PdGe phase. The 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 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 Andrew Thust

Wednesday, December 1, 1999
8:00 PM
Exhibition Hall D (H)

Q4.1 SLIP PROPAGATION AND SLIP-STEP INTERACTIONS STUDIED BY LEEM W. Swiesh, M. Mundschau 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 (1120) 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 structure defects influence surface topography. 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. B. 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 electron microscopy (SAEM), because up to now finite beam sizes of the order ~1-1.3 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 (~15-20 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-like profiles that capture surface topography 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 (r) = (1-4ab(b)) , where r represents the roughness fluctuation along a lateral-in-plane 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 smaller than x, with x a peak correlation length that was comparable to average specimen cluster sizes. Experimental observations are presented for pure AI 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 (< 5 kV) operating voltages can lead to an order of magnitude improvement in spatial resolution relative to the approximately one micrometer resolution achievable at ~30-50 kV operating voltage 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 the pixel size reduces 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 (~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 (~10 by 10 MByte) raw data files will also be discussed. Research at the Oak Ridge National Laboratory SbRE 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. Pagworth, 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 carbides, 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-ray maps can detect these small precipitates, but take time to be evaluated.

M. Watanebe et al. has implied that with the use of the Σ 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. Peaks 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 concentration has been developed and has proved to be surprisingly accurate.


Q.4.5

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

Uranium compounds relevant to contaminated soil were studied by electron energy loss spectroscopy (EELS). Core-loss EELS results suggest that uranium 4⁺ compounds have an energy loss resolvable from 6⁺ compounds. Cationic characteristics distinguish carbon-free uranium oxide specimens on silicate 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.

Q.4.6

**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 usual electronic and magnetic properties. However, in this work we are interested in the association of NiS with the spent anode fraction of toughened glasses, where the NiS inclusion is found on a fracture surface at the initiation-of-fracture point. Fracture of toughened glasses occurs when NiS inclusions in the hexagonal (alpha) state transforms 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 5 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 remnant strain in the transformed grains or it may be that high resolution TEM images are very sensitive to crystal misalignment.

Q.4.7

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

With developments in hardware and data processing, the technique of orientation imaging using electron diffraction techniques has become very popular. The full value of such techniques however require that there is enough resolution to detect the varying levels of rotation that occur within microstructures. 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.

Q.4.8

**STRAIN ANALYSIS WITH LARGE-ANGLE CBED**
Helge Heinrich, Alessandro Vanzet, 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 experiments are compared with dynamic large-angle 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 γ-phase of lamellar two-phase TAI/TAI Al-AlSi12 alloys are imaged in (001) planes. With two weak-beam images of an Σ2 lamella, one component of the resulting strain field can be evaluated quantitatively. The strain fields are compared with data obtained from LAED. If the a2 lamellae exceed a thickness of about 200nm, they efficiently shield the stress fields induced by the deformation twins in the γ phase.

Q.4.9

**HIGH SENSITIVITY CONVERGENT BEAM ELECTRON DIFFRACTION FOR THE DETERMINATION OF THE TETRAGONAL DISTORTION OF EPIAXIAL FILMS**
Christen Scher, Markus Leicht, Thomas Marek and Horst P. Strunk, Institute for Microchemistry, 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 ability to yield a spatial resolution of typically 10nm. However, the sensitivity of 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 (HRXRD) offers a higher sensitivity to lattice parameters, but its results are averaged over several micrometers of film thickness. Our aim is to determine with high spatial resolution the tetragonal distortion of GaAs epitaxial layers which are 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 Δc/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) disk 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 Houck 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. Reference [1] D.B. Williams, C.B. Carter, Transmission Electron Microscopy, Vol. 2 Diffraction, Plenum, New York (1996) [2] X. Liu, A. Prasad, J. Niragio, E.R. Weber, Z. Lichtenfeld, W. Winkelmann, Appl. Phys. Lett. 67 (1995) 279.

Q.4.10

**DETERMINATION OF COHESION STRAIN FIELDS AROUND COHESIVE PARTICLES IN Ni-Al ALLOYS BY HREM AND CBED**

Quantitative evaluation of cohesions strain around particles in the alloy Ni-12 wt%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 incommensurate elastic functions and in some cases form groups of many particles. HREM has been used to acquire images including the particle matrix interface. The selected zone axis is [001]. The quantitative analysis to determine the positions of the intensity minima and the subsequent evaluation of the contrast parameters, is made by using the software Dapir. 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 [Prog. 28062U] and COFAA-IPN.

Q.4.11

**TEM STUDIES OF UNUSUAL MICROSTRUCTURES WITH INTERNAL LATTICE BENDING FORMED IN CRYSTALLIZED AMORPHOUS FILMS**
Yuliya Yu. Kaluga, Yinxiang Yang, Akira Takahashi, Ural State Economic Univ., Engineering Dept., Beterburg, RUSSIA; Anders R. Tholen, Chalmers Univ of Technology, Dept of Experimental Physics, Göteborg, SWEDEN.

Amorphous films and thin layers have various areas of applications (e.g., in microelectronics and information storage) and their crystallization (either undesirable or desirable) is of prime interest. Nanometer scale bend contours were often inherent in micrographs of crystallized areas. It was shown earlier that they correspond to unusual microstructures with strong (up to 120° per micron) regular, dislocation independent internal bending of the crystalline 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 scanning CCD camera. EDX, EELS and CBED are also used. For the crystallization 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 intensity and geometry and grain boundary density, are strongly increasing, whereas the growth rate is going to and including zero. Crystal growth of hexagonal Si in Nb-Te films with a gradient in relative concentration of elements was studied in the amorphous parts, enriched with Si. The magnitude of internal stress in Si crystallizes (for the growth rates in the range 0.5 - 1 µm/s) is built up upon the increase of Te content in amorphous film. HREM re-examined all the studies with results for iron oxide and iron crystallizing rhythmically with alternation among zones of different contrast and imperfectness. Most perfect and imperfect regions and the amorphous-crystalline interface at the moving crystallization front were examined.I. Kolesov, V. Yu, Proc. XII IEM, Seattle, San Francisco Press, v. 1, 574 (1990). This work is partially supported by RAS grant 1557 and RFBR grant 97-03-17784.

Q.4.12 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. After electron microscope 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-beta titanium aluminides and potential factors for improving the high temperature strength.

Q.4.13 SPECIMEN CURRENT IMAGING OF DELAMINATION IN CERAMIC FILMS ON METAL SUBSTRATES IN THE SEM. Srinivasa Ranganjvan, 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 sputter. Constraint due to adhesion at their interface generates sufficient stresses during cooling from the melting point to substrate temperature that cause delamination. Stress relief by cracking is always accompanied by delamination of the thin film 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 detecting regions of the specimen due to cracked segments of a sputter. Image analysis using this contrast provides a qualitative measure of the extent of delamination at the interface. Study of sputter on substrates at different temperatures reveals greater delamination at lower temperatures. Correlation also indicates complimentary nature of stress relief by delamination and cracking. A detailed analysis including data from solubility of cooling during cracking and cracking statistics will give a measure of the adhesion strength at the interface. This technique is a rapid method for measuring delamination of macroscopic scale in thin films on conducting sputters. Acknowledgement: this work is supported by the National Science Foundation, MRSEC program, Grant No. DMR 9822372.


In the present work, transmission electron microscopy was applied to the studies of structural and morphological characteristics in situ in interaction in metal systems. For this purpose, the pairs of interacting elements were chosen so that 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, Nb-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 a crystal particle in the matrix. 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 approximate state of the reacting substances, the nature of transported particles and the way 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 microanalytical observations of the interaction allowed us to make conclusions concerning the formation and the development of the defect structure at the interface boundary between the interacting substances.


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-Pi-Sn eutectic alloy, Al-Cu eutectic alloy and alumina. Structure and dynamical behavior of a liquid-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 a nanometre map in the liquid phase near a solid-liquid interface.

Q.4.16 SITE OCCUPANCY DETERMINATION BY ALCHEMIST OF Nb AND Cr ALLOYING ELEMENTS IN GAMMA TITANUM. ALUMINIDE JAMES WANG, M. E. B. Kim, University of Tennessee, Memphis; T. W. Anderson, Oak Ridge National Laboratory, Oak Ridge, TN.

The site distributions of Nb and Cr alloying additions have been characterized in the Li2O-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 solidification temperature in the gamma single-phase field and water quenching from the gamma-beta 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, hence the two sublattices are distinct as expected. Significant 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.

Q.4.17 ELECTRON CHANNELING X-RAY MICROANALYSIS FOR CATION CONFIGURATION IN IRRADIATED MAGNESIUM ALUMINATE SPINEL. Yu. Matsuk, K. Tsuoi, J. Kinbara, Kyoto Univ, Dept. of Applied Quantum Physics and Nuclear Engineering, Fukuoka, JAPAN; N. Zuev, Materials Science Division, Argonne National Laboratory, Argonne, IL.

Magnesium aluminate spinel compounds (MgO/Al2O3) 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/Al2O3, Mg2+ and Al3+ 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 O2- ions. The reliable stability in radiation fields is believed to be 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/Al2O3. In the experiment, TEM specimens of MgO/Al2O3 were annealed at 1470°C for 48 hours under the beam at 870 K to a dose of about 2 dpm with 1 MeV N2 ion or 900 kV electron. X-ray emission from the specimens was measured as a function of
electron beam rocking between 16.0 and 16.0 Bragg positions at an accelerating voltage of 120 or 200 kV. In unirradiated or undamaged areas, rocking curves of characteristic core emission show strong dependence on the diffraction condition of incident electrons. They suggest that about 80% of Mg2+ ions and about 90% of Al3+ ions are located on Ti-sites and Os-sites, respectively, while the rest are on the other subsites. The characteristic core emission becomes less dependent on the diffraction condition for damaged regions, owing to disordering. In regions irradiated to 2 dpa with 900 keV electrons, Mg2+ ions on Ti-sites and Al3+ on Os-sites decrease to about 60% and 80%, respectively. Most 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. Anantharao, B. Baverjee, Hanadi L. Frase, Ohio State University, Dept. of Materials Science and Engineering, Columbus, OH; S. Baverjee, Materials Group, Bhilabhr 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 common ordering schemes in intermetallics is the B2 structure which divides the bcc lattice into two primitive cubic sublattices. In binary B2 alloys, the long range order (LRO) may be described in terms of a single LRO parameter which makes the description of the ordering 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 Ni3Ta-Al system as well as Fe-Al and Ni-Al systems with ternary additions. Atom location by channeling enhanced microanalysis (ALCHEM) 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 1.5 beam approximation. In addition, the OTLs have been calculated using a model based on 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 experimental results will be presented emphasizing 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 Naeck and Eberhard Schaed, 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°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 small amounts of Mn, CaO and Y2O3 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 monocrystalline ZrO2 in NH3 at elevated temperatures. We have used time 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 reveals that Mn 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

Chair: Dean J. Miller, Ray D. Twisten and Yamei Zhu
Wednesday, 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 Vignesh P. Dressel, Northwestern Univ, Dept of MSE, Evanston, IL.

With shrinking dimensions of devices and associated phenomena, it has become necessary to manipulate and analyze materials structures at a 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. Although 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 (<10-20 nm) coupled with ion-beam current for sputtering and deposition. In TEM community, however, FIB are often associated with thin foil sample preparation, especially for difficult materials systems (e.g. composites, metal-semiconductor systems etc.) where traditional ion beam thinning (IBT) suffer in making wafer scale cross-sections. Hence the site-specificity of FIB and its ability to sputter.deposit a wide range of materials has opened several niche and unusual applications. This presentation will cover not only the traditional role of FIB in making transparent TEM foils for different applications but highlight some emerging and niche applications in nano/micro manipulation.

The great ability of modern FIB in making site-specific thin sections will be demonstrated for ceramic nano-composites (CNMs), where conventional steps (IBT) suffer in applying to the differential thinging, cracking and drop-outs of weakly bonded films. 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 microfluidic dynamics, site-specific electrode deposition, AFM tip synthesis etc. will be presented.

Q5.2
TEM SAMPLE PREPARATION USING FIB/SEM DUALBEAM TECHNIQUE. Seng Da, Y.C. Weng, FEI Company, Hillsboro, OR.

Nowadays, semiconductor structure has been constantly shrinking to a much smaller feature size (~0.25-1.0μm). The use of FIB (Focused 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 unintended 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 Teachin, FEI Company, Hillsboro, OR; Efraim M. Reznik, 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 to evaluate the wafer fab, however, the most important to detect and electrical defects must be characterized out of the fab in the lab environment. With current semiconductor technologies typically less than 0.25μm, it is becoming increasingly difficult to achieve sub-micron accuracy, on a consistent basis, using mechanical polishing or manual cleaning 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.
Electron Microscopy) imaging in a dual beam (FIB/SEM) workstation. The MC200 microscope (Newcastle University) was used to prepare the sample for analysis. The sample was then examined in the SEM column. The SEM images were taken at an accelerating voltage of 15 kV and a working distance of 10 mm. The secondary electron images were acquired using a SEM chamber at an operating pressure of 1 Pa. The sample was then transferred to the FIB column for further analysis.

Q.5.4 ENVIRONMENTAL-SCANNING ELECTRON MICROSCOPY AS A TOOL FOR MICROCRACK STUDIES IN CONCRETE
Jan Bischop, Jan van Mier, Delft Univ. of Technology, Dept. of Civil Engineering and Geosciences, Delft, THE NETHERLANDS.

During the hardening of concrete the concrete fraction shrinks due to the 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 it is considered a very promising tool for the quantification of shrinkage microcracking. In ESEM concrete samples can be examined at relative humidities of 99%, 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 inside the chamber. At different intervals during drying ESEM-samples are prepared and a map of the permanent 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 before the sample surface. The results of the experiments are presented in detail in a presentation.

Q.5.5 MICROCHARACTERIZATION OF COMPLEX SPECIMENS OF ENVIRONMENTAL INTEREST CONTAINING TERRA DUST
DEVELOPMENT OF SPECIMEN PREPARATION METHODS AND ANALYTICAL PROCEDURES
Marina Caminati, Gian Corbetto, Giovanni F. Crosta, DISAT, Università di Milano Bicocca, Milan, ITALY, Giuseppe Galini, Pierelli Pneumatici, Milan, ITALY, Tigran Doshkianyan, Changmo Sung, Dept. of Chemical Engineering, University of Massachusetts-Lowell, Lowell, MA, USA.

Particulates produced by automotive traffic contained complicated species such as combustion products and debris from the wear of brakes and tires. 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 X-ray, 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. In the present SEM and TEM analyses were properly combined with EDX and ESEM techniques along with sophisticated sample preparation methods.

Q.5.6 INCOHERENT HIGH RESOLUTION Z-CONTRAST IMAGING OF SILICON AND SILICON-ARMED ARSENIDE USING HAADF-STEM
Yasuhiro Kozaki, Yoshio Kikuchi, FUJITSU LABORATORIES LTD, Kawasaki JAPAN; Takashi Yamazaki, Department of Physics, Science University of Tokyo, Tokyo JAPAN; Kenzou Watanabe, Tokyo Metropolitan College of Technology, Tokyo, JAPAN.

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

SERVING TO PROVIDE INCOHERENT IMAGES OF CRYSTALLINE MATERIALS WITH STRONG COMPOSITIONAL SENSITIVITY DEPENDENT ON ATOMIC NUMBER. Z-CONTRAST IMAGES AND HIGH RESOLUTION ELECTRON MICROSCOPY SHOW DIFFERENCES IN THE ELECTRON TRANSPORT LEVELS OF DIFFERENT MATERIALS. THE STEM TECHNIQUE IS COMPATIBLE TO THE CONVENTIONAL ELECTRON MICROSCOPY (HRTEM).

Q.5.7 THE ATOMIC STRUCTURE OF MOSSBAUER GRAIN BOUNDARIES DISLOCATIONS IN GaN EPITAXIAL LAYERS
Valerie Potin, Gerard Néel, Pierre Jarrett, Ecole Normale Supérieure, Recherches sur les Materiaux, UPRÉSA CNRS 6001, 15MA, Cen, 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. Present high resolution electron microscopy, microdiffraction electron microscopy, and high resolution electron tomography are used to reveal the atomic structure of these dislocations. In addition, theoretical simulations have shown that the density of high angle grain boundaries is significantly lower than that of low angle grain boundaries. The results have been compared with the experimental data and the agreement is found to be good.

Q.5.8 INTERFACE STRUCTURE AND Zn DIFFUSION IN CdTe/ZnTe/Si SYSTEM GROWN BY MBE
J.C. Tauc, P. Czirják, J. Kociak, Arizona State Univ., Center for Solid State Science, Tempe, AZ, USA; R. Rajamathi, S. Sivanathan, Univ. of Illinois at Chicago, Microphysics Laboratory, Department of Physics, Chicago, IL, USA.

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 into the CdTe, a high-resolution field emission gun SEM with an atomically resolved imaging capability was used. The local atomic structure of each sample was studied using high resolution electron microscopy. The results were compared with the theoretical predictions and the agreement is found to be good.

The use of a high angle annular dark field (HAADF) technique in a dedicated scanning transmission electron microscope (STEM) is
interfacial planes 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. 
Sanjiv Singh Dugg, Teja T. Taparia*, Nigel D. Thompson* and Christopher G. Tchernia, 
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 (≤5 nm thick) becomes critical for performance of gate and tunnel dielectrics in metal-oxide-semiconductor field effect transistor (MOSFET) and electrically eraseable programmable read-only memory (EEPROM) structures, respectively. But boron (used to dope polysil to form p+ gate) can penetrate through thin oxides into the channel region, leading to degradation of the electrical properties. With the incorporation of silicon nitride 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 nitrogens distribution in these films with high spatial resolution 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. The atomic-scale imaging (≤2 Å) of this study might 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 ultrathin dielectrics.

Q5.10

TANTALUM AS DIFFUSION BARRIER LAYER BETWEEN COPPER AND Si: FAILURE MECHANISM AND EFFECT OF OXYGEN. 
Kai-Min Yin, Pei-Rong Chen, Ji-Jung Kri, Dept of Engineering and System Sciences, National Tsing Hua University, Hsinchu, Taiwan; ROC; Peijun Ding, Barry Chen, Hong Zong, Fusan 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 penetration through barrier layer at various high temperatures anneal. The thin films Ta25nm/Cu5(15)nm were deposited onto Si substrate using ionized molybdenum plasma technique (IMP) process under ultra-high vacuum condition (~1 x 10^-7 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 normally diffuses through the grain boundaries of Cu films and reacts with Ta film to form amorphous TaOx film between the interface of Cu and Ta. At 600°C, Ta and Si first react into Ta2Sn, then the Cu diffusion transformed the structure of Ta2Sn to Ta3Sb2 and both n’ and n” Cu/Si phases would form in Si substrate. At 600°C, oxygen from outside atmosphere could also diffuse through Ta films and oxides part of Cu/Si to form silicon dioxide. This report proposes that the existence of n’ and n” Cu/Si phases after 600°C can be due to the oxygen process of the slow phase transformation from n’ to n”. This result is in contrast to some previous observations only one n” phase exists in high temperature.

Q5.11

TEM AND HREM STUDY OF BLISTERING IN HYDROGEN IRRADIATED SILICON LAYERS ANNEXED AT HIGH PRESSURE. 
T. Poppa, A. K. Ochota, A. I. Antonov, Institute of Semiconductor Physics, Novosibirsk, Russia; A. Moroney-Rodrigues, A. Bahrouiri, University of Barcelona, Department of Electronics, Barcelona, SPAIN; A. Minnik, Institute of Electronic Technology, Warsaw, POLAND; J. S. Minnik, Institute of Physics, Warsaw, POLAND.

Hydrogen implanted silicon layers have been successfully used for Silicon On Insulator (SOI) creation. Fundamental phenomenon of blistering at the interface has been in the focus since the 1970s. The 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 interstitial (I). Their concentrations are only slightly larger than implanted H atoms. These defects can annihilate, cluster, and lead to the formation of highly conducting platelets with intersecting plates during irradiation. It was supposed that HV1 and HV2 defects move fast to platelets, and annihilate at their walk leading to an increase in H2 gas content inside the extended defects and their growth at annealing with constant gas pressure 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 ion 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 Y2O3:Eu THIN FILMS ON LaAlO3 SUBSTRATES. 

Yttrium oxide (Y2O3) 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 electro-luminescence devices. Transmission electron microscopy (TEM), x-ray, and Z-contrast scanning transmission microscopy (Z-STEM) were employed to relate the microstructure, interface structure, and cathodoluminescent (CL) properties of the Y2O3:Eu thin films deposited. Due to the 185 Å lattice mismatch, epitaxial growth of Y2O3:Eu thin films was obtained on LaAlO3 (001), with the orientation relationship [110]Y2O3//||[001]LaAlO3 and [110]Y2O3/[001]LaAlO3. STEM imaging of the films shows the Y2O3:Eu always remains aligned with the Al substrate. No Eu precipitates were observed. The Y2O3:Eu thin films, although good single crystals, contain a large density of small pores, which strongly affect their luminescent properties. It is known that surface 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 on a 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

Chair: 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.
Athena M. Donald, Bradley L. Thiell, Debbie J. Stokes, Ian C. Bedne, Robert G. Milhers, Cavendish Laboratory, University of Cambridge, UK.

Environmental Scanning Electron Microscopy (ESEM) obviates the need for conductive coatings to be applied to insulators in the presence of gases 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 a heterogeneous material is due to inelastic scattering in the H2 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 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. Libert, 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 width of this balance is such that the tube is often 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 to such interfaces. This is the main reason why they have been carried out mainly in the 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 widths of polycrystalline [poly(styrene)] [PVP] dispersed in poly(styrene) [PS]. The measurement determines the fraction of nitrogen, characteristic of the PVP phase, as a function of position on the PS matrix. The effective interfacial width for electron beam 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 agreement with independent measurements by neutron scattering. Dose-studied regions show that mass loss during the electron beam 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 ± 0.20. The stoichiometric value is 7.0. The presentation concludes with brief mention of parallel studies of interphases in fiber-reinforced resins based on spatially-resolved energy-loss measurements of local acrylonitrile.

9:15 AM Q6.3 TRANSMISSION ELECTRON MICROSCOPY IN BIOMIMETICS. Mohamed Sukiyan, 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), molluscan shell structures, proteinaceous and echinoderm skeletal units, sponge spicules, and bacterial and viral ultrafine particles, have unpretentious microscopic (mechanical, magnetic, optical) properties, developed over 3.5 billion years of evolution. These properties result from highly ordered nano- and microstructures of biological composites that self-assemble, often, into hierarchical architectures at ambient conditions for 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-mimicry and bio-functionalization. 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. Further, since biomaterials have hybrid structures, i.e., composites of biomacromolecules (proteins, polysaccharides, and lipids) and biominerals (such as CaCO3, CdS, Fe3O4, and SiO2), 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 (thin-lamella prepared by the Arctica method), nanoindentation, and EELS spectroscopy techniques. The biomaterials to be discussed include nanohydrated composites and their local dielectric functions in molluscan shells [piezoelectric], ordering of magnetic particles in magnetotactic bacteria (magneto-cocoon coherent ceramic precipitates in rhizopathogenic fungi (magnetite), the nature of impurity silicas in sponge spicules (optical), and ultrafine hydroxypatite crystals 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 biomaterials science applications.

10:15 AM Q6.4 MEASURING THE PHYSICAL PROPERTIES OF INDIVIDUAL NANOSTRUCTURES BY IN-SITU TEM. Z.L. Wang, School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA.

Nanomaterials have distinctively different properties from bulk because of their unique crystal and electronic structures. Characterizing the physical properties of individual nanomaterials, 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 nanomaterials. Using in-situ transmission electron microscopy, we have developed a carbon nanotube has been observed in-situ in TEM, confirming the ballistic conductance and no-hem dissipation across a defect-free nanotube [1]. In-situ measurements on the mechanical properties of carbon nanotubes have been carried out 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 method has been used to study 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 method has been used to study 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.
11:15 AM Q6.8
EPITAXY AND ATOMIC STRUCTURE DETERMINATION OF Au/TiO2/INTERFACES BY CO-BROXED EBSD AND HRTEM. Frederick B. Smith, 1-2 J. C. G. Poole, 1* and James M. Robertson, 1* 1Department of Chemistry, 2Department of Materials Science, University of Bath, Bath, England, UNITED KINGDOM.

The Au/TiO2 system is of importance in catalysis, because of its high activity for low temperature oxidation of CO and its good sensitivity as a CO gas sensor. This is caused in part by a unique yet unknown synergistic effect between the Au aluminas and the TiO2. The effect of substrate temperature on the epitaxial orientation relationship of Au islands on TiO2(110) has been determined by high spatial resolution electron backscatter diffraction (EBSD). In addition, we have examined the atomic structure and chemistry of Au/TiO2 interfaces by high resolution transmission electron microscopy (HRTEM). Upon increasing growth temperature from 300K to 775K, the epitaxial orientation relationship of Au islands on TiO2(110) changes from (111)Au to (112). This plane orientation with the same < 110 > Au/TiO2 direction. In both cases, the epitaxial orientations are observed. The Au/TiO2 interfacial structure and chemistry of these two epitaxial orientations have been determined by HRTEM. The epitaxial orientation results are explained in terms of stoichiometry of TiO2(110) interface and Ti-Au interfacial bonds.

11:50 AM Q6.9
THEORETICAL EXPLANATION OF PT TRIMERS OBSERVED BY Z-CONTRAST STEM. Karl Schütrumpf, 1* S. R. S. Plumb, 2 A. J. F. Venter, 3 A. J. L. Blythe, 1 Karlsruhe Institute of Technology, Karlsruhe, Germany, 2University of Texas at Austin, Austin, TX, 3University of Cambridge, Cambridge, United Kingdom.

First principles quantum-mechanical calculations on γ-alumina have revealed a fascinating 'reactive sponge' phenomenon. γ-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 γ-alumina support showed individual atoms to form dimers and trimers with preferred spacing and orientations that are apparently dictated by the underlying support. [Nellist and Pennycook, Science, 274, 413 (1996)]. In turn, the reactive sponge property of γ-alumina is the key to understanding the Pt clusters. Our calculations demonstrate that if three Pt atoms form 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 HRTEM AND MOLECULAR DYNAMICS. M. José, 1* J. Acosta, 2 Yacaman, 1* S. Tellez, 1* 1Departamento de Química, Universidad de los Andes, Bogota, Colombia, 2Instituto de Investigaciones del Petróleo, Mexico, MEXICO.

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 catalysis all the active atoms are accessible for the chemical reactions. However traditional TEM fail to show a structure consistent with the chemical data. In the present work we study the case of Pt-γ-Al2O3 catalyst which is widely used in reforming in naphtha. We used molecular dynamics simulations and quantum mechanics approximations to study the structure of γ-Al2O3 and the interaction of Pt atoms with the vacancies on the alumina. The resulting model was used to simulate HRTEM of images of the particle structure. These simulations provide a guide to understanding the structure of the Pt clusters. In particular it becomes clear the role of the γ-Al2O3 which acts as a Supersponge and the formation of clusters inside the γ-Al2O3 matrix.

SESSION Q7: INTERFACES IN METALS AND CERAMICS I
Chair: Robert J. Gottschall and Robert Hult
Thursday Afternoon, December 2, 1999
Salon A/B (M)

1:30 PM Q7.1
THE USE OF THE FOCAL SERIES RECONSTRUCTION
Precipitation in supersaturated mixtures of transition metal borides in the system Ti$_2$W$_2$B$_6$-C$_6$H$_6$ leads to particle-strengthened hard materials. The structure and chemical composition of two types of precipitated phases was studied by means of X-ray diffraction analysis on model samples. The precipitates are thin platelets (0.1 mm thickness) lying parallel to the (100) prior phases. Lattice images yield precipitate thickness and lattice displacements of the metal positions with respect to the matrix, which uniquely depend on the precipitate thickness of the W$_6$B$_4$ 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 precipitates show a decrease in the B and Ti concentration, whereas the W concentration increases and the Cr is homogeneously distributed. The HIETEM results combined with the results of the elemental maps can be explained by a structural model based on the intergrowth of the ABW structure in the Ti$_2$B$_4$ 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$_{0.5}$Ti$_{0.5}$. The double deficient boron layers in W$_6$B$_4$(Ti,B) with a spacing of 0.38 nm can be used to measure the thickness of the precipitates. In the boron jumbo-ratio image of W$_6$B$_4$(Ti,B) two dark lines are clearly resolved indicating the deficient boron layers. The chemical origin of this contrast is critically discussed.

**3:30 PM Q7.5**

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

In many Al- or Mg-based metal matrix composites, reinforced with SiC, Si$_3$N$_4$, or Al$_2$O$_3$, a thin (1-3 nm) amorphous film is commonly observed at the matrix and the reinforcing phase. In SiC or Si$_3$N$_4$ reinforced systems, the Si-rich amorphous phase is formed from the precursor (natural) oxide film at the surface of the SiC and Si$_3$N$_4$. However with Al$_2$O$_3$ reinforcement, an amorphous phase only forms when certain key alloying elements (Si, Mg, and Sr) are present in the Al matrix alloy. In this presentation I will highlight the role of analytical electron microscopy in unravelling the structure and composition of the films, using a JEOL 1010 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. HIETEM has been used to measure the thickness of the films and to reveal their “winding” characteristic of the amorphous phase at the junction of two reinforcing particles. For Al$_2$O$_3$ reinforced alloys, Si 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. Reul, Metallurgy 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 (IASC C) of neutron-irradiated austenitic alloys has been attributed in part to radiation-induced segregation of both major and minor alloying elements, especially Cr and Ni, to grain boundaries. The segregation is associated with the low irradiation temperature ($\approx 570$ K), the segregation profiles are very narrow (less than 5 mm) and require the high spatial resolution of a field emission gun scanning transmission electron microscopy (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 fluence. The segregation evolves from Cr and Ni-enrichment at grain boundaries prior to irradiation to W-shaped Cr profiles at $\approx 1$ dpa (displacement per atom) to conventional Cr depletion profiles with increasing dose. This redistribution is accompanied by an enrichment of Cr$_{\text{Im}}$ at grain boundaries. The impact of pre-irradiation segregation on subsequent RIS and the role of RIS on IASC C will be discussed. Research sponsored in part by U.S. Department of Energy, Division of Materials Sciences, under contract DE-AC05-76OR00032 with Lockheed Martin Energy Research Corp. and through the SHARE User Program under contract DE-AC05-76OR00032 on the Oak Ridge Institute for Science and Education. Research in the SHARE and Research Equipment (SHARE) User Facilities at Oak Ridge National Laboratory.

**4:15 PM Q7.7**

**SUBSTITUTIONAL IMPURITY SEGREGATION TO THE $\Sigma$3(10) / [001] STGB IN FCC METALS.** Jaeger M. Plazzio, 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.

Investigation of the $\Sigma$3 symmetric tilt grain boundaries (STGB) in face-centered cubic (FCC) metals was performed. The metals we have chosen include pure Aluminum, pure Copper, Copper with 1 at% Silver, and Aluminum with 1 at% Copper. The model grain boundaries have been fabricated with ultrahigh vacuum diffusion bonding of single crystals. The atomic structure of the Sigma 3 (310) / [001] STGB for the different metal systems was modeled with atomic 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 proof 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 was obtained by determining the atomic positions of the segregated atoms at the interface. HRTEM coupled with image simulation and reconstruction of through-focus 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 Sigg, Li-Shin Chang, Wolfgang Gurt, Manfred Rüüle, 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 phase diagram. By means of Auger spectroscopy Cu$_{\text{Im}}$ and Bi coincidence was found for wetting of GBs within the one-phase regime of the volume phase diagram [3]. In the present work segregation at a specific high energetic GI (319) 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 diffusional 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 pro-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. Müller, and M. Rüüle, to be published in Acta Met. [2] L.-S. Chang, B.H. Straumal, E. Rabin, W. Gurt, and F. Sommer, J. Phase Equilibria 18 (1997) 128. [3] L.-S. Chang, E. Rabin, B. Straumal, P. Lejcek, S. Hofmann, and W. Gurt, Scripta Mater. 37 (1997) 729.

**4:45 PM Q7.9**

**MEASUREMENT OF THE ATOMIC STRUCTURE OF BISMUTH DOPED COPPER $\Sigma$5 GRAIN BOUNDRIES.** Thomas Ggemmer, Uwe Alber, Manfred Rüüle, 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 atomic-level 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 analyze the structure of $\Sigma$13 (013) [011] grain boundaries in pure as well as in bismuth doped copper. HREM using the JEOL ARM250 installed in Stuttgart allows an atomically resolved phase contrast
SESSION 8 PAPER SESSION - PARTICIALLY ORDERED AND NONPHASE MATERIALS

Chair: Colin Peter Flynn and Mehmet Sorukaya
Thursday Evening, December 2, 1988
8:00 P.M.
Exhibition Hall D (H)

Q8.1 LOW DOSE HREM IMAGING OF LATTICE CURVATURE IN TWISTED MPE POLYMER CRYSTALS
Christian Koehler, Daniel P. Lawrence and David C. Martin,
The University of Michigan, Materials Science and Engineering, Ann Arbor, MI.
Poly(m-phenylene diphenylamine) (MPE) is a wholly aromatic polymer used to manufacture thermally stable fibers (Nomex by DuPont). When MPED-MPE-DAC solutions are slowly crystallized by exposure to air (water vapor), the crystallites precipitate into uniform, regularly twisted crystalline bundles. Here, we examine the internal structure of this remarkable material at high resolution. HREM images have been obtained for plates 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 local distortions of the crystal lattice. Electron diffraction patterns reveal a symmetry that is substantially different from that of the model proposed by Kakihana et al. (1976) for the commercially spun MPE fiber. Computer-generated models for the crystal structure will be shown and compared with the available experimental TEM and SAED data.

Q8.2 ELEMENT COMPOSITION IMAGING OF NANO SOLIDS IN SOLUTION
Jan-Olov Rinse, Gunnel Karlsson, Jan-Olle Malm,
Oliver Hammar, Torsten Hubler, 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, ionic exchange, structure determination of solids in equilibrium with solutions, etc. Vitrification of the liquid phase, on the TEM grid, was achieved by plunging the vapor phase of the vitrified samples 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 Bi-TWIN 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 instantaneously scattered electrons can be used to record jump ratio elemental maps in less than a minute. The same is true 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 the jump ratio maps could be recorded from the same spec a and the twin-defects indicate an image-resolution of about 2.5 nm. It is shown that it is possible to freeze thin films of methanol, ethanol and tetrahydrofurane (THF). It was found that frozen methanol was more stable than the same time HREM the frame work was not stable. 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
Terry Gibson, Argonne National Lab, Materials Science Div, Argonne, IL.
Ji-Xin Cheng, Paul Voyles, Univ of Illinois, Dept of Physics and Materials Science, Urbana, IL.

Michael Tracey, 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-conference transmission electron microscopy). This technique is sensitive to medium-range order structures. The results on ion-implanted samples showed a striking similarity of evaporated amorphous silicon. We found that both ion-implanted and evaporated samples have a crystalline structure, rather than continuous random-network structures. We are also studying the 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 stress 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 CHARACTERSIZED 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 sp3 bonding. Correlations of bonding and properties are important for optimizing coatings for specific applications. Cross-sectional TEM specimens of DLC thin films that have been ion implanted after plasma deposition have been studied. Ratios of sp2/sp3 bonding have been measured from electron energy-loss spectra (EELS) with established methods that are based on the relative intensities of sp2 and # bonded at the carbon edge, and beam damage that can be encountered with focused probes, high-resolution spectra were acquired in the TEM mode with a Gatan imaging filter (GIF) interfaced to a Philips CM300. The method employs a simple slit in the GIF entrance aperture and the use of a specimen rotation holder. Nonlinearized spectra in increased sp3 bonding and 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 p to sp2 ratio. Namely 2-4% wide-slit were used to acquire an extended set of spectra showing the self-bonding and sp3 bonding maps.

Q8.5 ATOMIC-SCALE STRUCTURAL INVESTIGATIONS OF THE DIRECT NUCLEATION OF CUBIC BORON NITRIDE FROM S1+ HYBRIDIZED AMORPHOUS BORON NITRIDE UNDER HIGH PRESSURES AND TEMPERATURES
J.H. Frey, EPFL, Lausanne, Switzerland; J. Kwo, Brookhaven National Laboratory for Ultra-High Voltage Electron Microscopy (UHVEM), Osaka University, Osaka, JAPAN; National Institute for Research in Inorganic Materials, Tsukuba, JAPAN; H. Mori, UHVEM, Osaka University, Osaka, JAPAN.

By controlling the microstructure of the starting materials, i.e. by ball-milling a commercial hexagonal boron nitride (h-BN), 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 those of crystalline h-BN under similar HP-HT treatments. HREM and EELS clarified the nucleation mechanism at an atomic scale. It demonstrated that the c-BN phase nucleates directly from the sp3 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 phase transformation, but very similar to one of the proposed mechanisms 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 and c-BN, which are still under controversy.

Q8.6 ENERGY-FILTERED TEM IMAGING AND PEELS ANALYSIS OF
BORON NITRIDE AND CARBON NANOTUBES. Oleg Louie, Rodney S. Ruoff, Dept of Physics, Washington Univ, St. Louis, MO; Bert Harrell, C. Milton, William E. Burks, 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 transmission electron microscopy and 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/TiO2 CATALYST. Tatsuki Akiyoshi, Koji Takahashi, Susumu Tsukada, Masato Hara, 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 10 nm on a metal oxide support. Especially, interesting features have been observed in Au/TiO2 systems. The selective oxidation of ethylene to propylene oxide occurs only on amine TiO2 support, but not on rutile TiO2. 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 such characteristic behavior are not clearly understood.

We have studied the crystal structure and electronic structure of the Au/TiO2 catalyst by HR-TEM, EELS and HAADF-STEM. Some basic features were found. There was a preferential orientation between Au particles and amine TiO2, but not with rutile TiO2. This orientation relationship was consistent with the result predicted from geometrical consideration. EELS measurement was also done for 0K-edge EELS. Specific features induced by Au particles supported were not found yet. But the shapes of EELS spectra from TiO2 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^4 dependence on the diameter D of Au particles, however, those of oxide particles were weaker than the predicted value obtained from D^6 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. Jingyu Li, Mentor Corporation Research, Mentor 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 small electron range and the corresponding reduction in interaction volume, low voltage microscopy 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. Boccal, Charles M. Lakehart, Vanderbilt University, Department of Chemistry, Nashville, TN; Ed A. Korn, 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 heterogenous catalysts can result in improved catalytic activity and/or longevity. The preparation of bimetallic catalysts with specific metal/metal oxide 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 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. The results from several different bimetallic catalysts indicate that there is some compositional size dependence, this dependence is consistent with a loss of a volatile oxide species from the surface of the metal particles. Application of a mathematical model to compensate for this presumed metal 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 NANO-PARTICLES BEHAVIOR. J.A. Ascencio, M. Jose-Yacaman, 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 thiol, the passivated and arranged nanoparticles have been obtained successfully, however there is not enough knowledge about the behavior of the thiol molecules around the metal particles. In several reports we have shown partial results of HREM simulation as a tool to interpret images produced experimentally, on this work use the method to analyse and address more carefully the role of the thiol molecules. By applying high resolution electron microscopy observation and simulation techniques, both chemical 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 thiol around the particle and how these molecules are affected when the electron beam is concentrated.

SESSION 90 POSTER SESSION
INTERFACES IN METALS AND CERAMICS
Chairs: Ian M. Anderson, Nigel D. Browning and George C. Westerby
Thursday Evening, December 2, 1999
8:30 P.M.
Exhibition Hall D (H)

Q9.1
CHARACTERIZATION OF THE INTERFACE BETWEEN SAPPHIRE AND HEXA-ALUMINATE BY EXIT WAVE RECONSTRUCTION. B. Wiesler, A. Steinecker, W. Mader, Universitats 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 LaAlO4 (La: La5+; Nd3+) convert into LaAl1.4O3 at temperatures > 1500 °C by reaction with the underlying substrate leading to extremely smooth films. LaAl1.4O3 films, better described by the formula Ln2+-A17+,2O15-, with magnetostructure structure grow with [0001] || [0001] out-of-plane and [112] || [010] in-plane orientation relationships. The magnetostructure structure consists of spinel-like nano-blocks with interlayers containing La.

To determine the terminating layer at the interface we used electron 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 interface and were compared with the reconstruction 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 epitactic system (111) spinel || (0001) sapphire.
Q0.2 ATOMIC AND ELECTRONIC STRUCTURE: ANALYSIS OF Σ=3, 9
AND 27 BOUNDARY, AND MULTIPLE JUNCTIONS IN β-SiC
Koji Tanaka and Masanori Koyama, 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 Σ=3, 9 and 27
boundary, and triple and quadruple junction in β-SiC were studied
by HREM and theoretical calculation. Especially, the existence of the
varieties of structures of Σ=3 coincident twin boundary and Σ=27
was shown by HREM.
The structure of Σ=3 coincident 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 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.
Σ=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.

Q0.3 ELECTRONIC EFFECTS ON GRAIN BOUNDARY STRUCTURE
IN BCC METALS
Wayne H. Campbell, James Belsk
University of California, Lawrence Livermore National Laboratory, Livermore, CA.
Stephen M. Bates, 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
components comprising the crystal. Understanding the influence of electronic structure on defects is a key ingredient for
successful atomistic simulations of materials with more complicated
crystal structures than FCC. We have found that grain boundary
structures is a critical test for interatomic potentials. To that end, we
have fabricated the identical [310]/001) symmetric tilt grain boundary in three different BCC metals (Nb, Mo, and Ts) by
diffusion bonding precisely oriented single crystals. The structure of these boundaries was determined by high resolution
transmission electron microscopy. The boundaries have been found to
have different atomic structures. The structures of these boundaries have been analyzed 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.

Q0.4 STRUCTURAL STUDY OF A [100]45° TWIST PLUS 7.5° TILT
GRAIN BOUNDARY IN ALUMINUM BY HREM
M. Stepanczuk, School of Mines and Energy Development, and Department of
Metallurgical Engineering, The University of Arizona, Tucson, AZ.

A [100]45° twist plus 7.5° tilt grain boundary in aluminum 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 high
concentration of steps due to the 7.5° tilt from a perfect [100]45°
quasi-periodic misorientation. Occurrence of coincidence and pseudo-
coincidence 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
boundary determines the boundary structure.

Q0.5 ATOMIC STRUCTURE OF GOLD BOUNDARIES. C.J.D.
Heineken, Sheffield Univ. Dept of Electronic and Electrical Engineering, Sheffield, UNITED KINGDOM.

The characterization 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 boundaries and
low index axes are helpful 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 microparticles with unexpected low index
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
thicker film. High resolution images of the nominally 10um thick film
were recorded on the Stuttgart 125keV ARM with the 0.14um planes
falling with the 0.12um 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 analyze
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 more 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.

Q0.6 FCC TITANIUM IN MULTILAYERS: A CAUTIONARY TALE.
J.E. Bonsewich and D. Joestl, 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 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
deposited as an as-received sample form for the first time. These
results highlight the importance of coupling TEM techniques with
XRD for detailed structural analysis of multilayer systems.

Q0.7 MICROSTRUCTURAL CHARACTERIZATION OF METALS
TREATED FOR HARDNESS AND CORROSION RESISTANCE
WITH PULSED INTENSE ION BEAMS. T.J. Berk, 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 - 4um thick
spatter-deposited transition metal coatings, were treated in the
RHPP-1 accelerator at Sandia National Laboratories using H, He, C,
N, Ar, and Xe beams, with incident fluences up to 10.7 cm-2 and
cooling rates of 106 - 107 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 and depth into the
material. Composition changes were measured by microbeam energy
dispersive spectroscopy (EDS). Treated samples show a consistent pattern of grain refinement with a somewhat
consistent nano-scale microstructure of approximately 5-10nm.
A high density of pores or voids were observed in the treated 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

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using dark field and bright field TEM and quantitative intensity measurements from digital images of thin regions show that dislocation density is 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 in those samples. XTEM showed that there is no 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-AC03-76-SF00098.

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 CoPt(Pt) 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 CoCrPt(Cr, CoCrPtCr, and CoPtCr) CoPtCr media sputtered under various processing conditions, in order to understand the 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 past several years. Extracting quantitative information at a spatial resolution approaching 1 nm involved treatments for diffraction contrast, variations in specimen thickness, and closely spaced ionization edges. Intergrowth Cr segregation of grain width is commonly observed. Compositions for hundreds of grain boundaries can be readily extracted from a single concentration map. Traditional AEM measurements are too tedious 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 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-AC05-86OR22464 with Lockheed Martin Energy Research Corp., and through the SHARE Program under the National Science Foundation with Oak Ridge Associated Universities. Support from the Vanderbilt University Research Council and Konag Inc. is gratefully acknowledged.

Q.9.9 FORMATION OF ALN FILMS ON Ti/TiN ARC-LAYER INTERFACE WITH AL-0.5% Cu INTERCONNECTS EVALUATED BY XPS AND ENERGY FILTERED TEM J. Gao, J. Zhao, P. Smith, A. White, Advanced Micro Devices, Process Characterization Analytic Laboratory, Austin, TX.

The use of Ti/TiN anti-reflective coatings (ARC) in photolithography of aluminum metal interconnects 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 AlN composite at the interface between Ti/TiN ARC and Al-0.5% Cu interconnect was investigated. The effects of deposition temperatures for individual films and ensuing thermal cycling of the 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. Formations of AlN or AlN2 were found to depend on the thermal cycling history of the metal stack.

Q.10 EFFECTS OF DEPOSIT AND ALLOWING TEMPERATURE ON THE REASSIGNMENT OF Cu IN 0.5% Cu - AlTiN PL. Smith and J. Gao, 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 Spectrometly. Localized distributions of elemental Cu, AlCu and CuTiAl 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 and growth of CuTiAl intermetallics were greatly influenced by deposition temperature, thermal history and the competitive formation of TiAlN intermetallics.


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 similar 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 proportional to a derivative of the calculated density of unoccupied states onto partial waves $p_{\alpha}$ 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 $p_{\alpha}$ the direction of the incident electron beam plays an important role. We acknowledge the Volkswagenstiftung (Az 17/029) for financial support.

Q.9.12 INTERFACIAL INTERACTION BETWEEN Cr THIN FILM AND OXIDE GLASS. Nan Jing, 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 has been receiving wide spread interest in the past few years. In this study, Cr thin films were evaporated in high vacuum on silica substrates and then subjected to a heat treatment at 1273K dress in a heating furnace. The Cr film thickness was measured 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. Formations of AlN or AlN2 were found to depend on the thermal cycling history of the metal stack.

Q.9.13 FULLY QUANTITATIVE ANALYSIS OF INTERFACES IN CERAMIC MATERIALS BY SPATIALLY-RESOLVED EELS METHOD. Hsueh, D.J., Corporate, Ceramics Supercrystalline 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 systems as well as thoroughly evaluating the
detector property. This could lead to reliable separation of interface
signal from that 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
reasonable 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
speculated or other orienting boundary, the definition of grain boundary
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,*1,2, P.H.
Imamura1 J. Bentley1 and M.L. McCaffrey1
1Oak Ridge Institute for Science and Education, Oak Ridge, TN; 2Metals and Cermics
Division, Oak Ridge National Laboratory, Oak Ridge, TN; 3Dept. 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 (YSZ-3Y2O3)
and doped 8 mol% yttria stabilized cubic zirconia (8YSZ-CSZ)
specimens has been measured using high spatial resolution
energy-dispersive X-ray spectrometry (EDS). Additives included glass
(1 - 5 wt % silicate, 1 wt % lithium alumina-silicate, 1 wt %
barium-silicate, or 1 wt % borosilicate), and 10 wt % alumina. These
constituents, which were added to accommodate strain and
additionally impede grain growth in 8YSZ-CSZ, were chosen
due to their effect on the sintering and texture of these systems.
Spectrometry was performed using a QuantSPEC Vision integrated
acquisition system interfaced to a Philips CM200 FEG AEM. EDS
spectra lines (typically 30 points, 0.5 to 2.0 mm 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
lower probe current (~1.2 nm FWHM, 0.5 nA). Some spectra lines
were acquired with automatic correction for drift. The results of this
AEM study, and the correlations to observed mechanical properties
generate to superplasticity (fracture characteristics and high-
temperature tensile deformation behavior), will be discussed.

Q9.15
MICROSTRUCTURE OF SrBi2Nb2O9 AND SrBi2Ta2O9 EPITAXIAL THIN FILMS
Mark A. Zurbuchen, James Lutteri, Yunfa Jin, Aftab H. Carin, and Darnell G. Schlenm, The Pennsylvania
State University, Dept. of Materials Science, University Park, PA; Wei Tran and Xiqing Pan, The University of Michigan, Dept.
Materials Science and Engineering, Ann Arbor, MI

SrBi2Nb2O9 and SrBi2Ta2O9 thin films were grown by pulsed laser
deposition (PLD) on (110) Nb2O5 and on (100) and (110) SrTiO3.
The films were studied by high resolution transmission electron
microscopy (HRTEM) to determine the interface and defect structure.
(001) oriented films were grown on (110) Nb2O5 and (100) SrTiO3.
These c-axis oriented films consisted of many identically-oriented
epitaxial domains offset by some fraction of the unit cell c-dimension,
resulting in measurements of phase boundaries (OPs) between
domains. Causes of the misregistration of neighboring nuclei were
investigated. Clean film/support 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 interface phase (~150 Å thick) was observed in some
samples, and was determined to be β-Bi2O3. Subsequent adjustment of
the deposition films free of this interfacial layer. On (110) SrTiO3 substrates, an epitaxial SrBi2O3 electrode was grown
prior to deposition of the SrBi2Nb2O9. The SrBi2O3/SrBi2Nb2O9
interface rough (~150 Å), and the films displayed bilayer
SrBi2Nb2O9 grows epitaxially on (110) SrTiO3 and (110)
SrBi2Ta2O9/SrTiO3 with the (001) plane of the SrBi2Nb2O9 parallel to the
(100) planes of the substrate. Two of the three degenerate ways in
which this epitaxial orientation can occur were observed, and
determined by the SrBi2Nb2O9/A3O3 boundaries between these two
orientation variants was studied.

Q9.16
Mg(OH)2 DEHYDRATION: A LAMELLAR NUCLEATION
AND GROWTH PROCESS. Michael J. McKelvey,8 Rami Shmarra,* Andrew V.G. Chizmeshya,* Ray W. Carpenter,* and Ken Strebe,*
“Center for Solid State Science, Arizona State University, Tempe, AZ,
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 CO2 emissions can be overcome. Permanent and safe methods
for CO2 capture and disposal/storage need to be developed.

Mineralization of stationary source CO2 emissions as carbonates can
provide such an approach to carbon long-term sequestration. Mg(OH)2
dehydration is a leading process candidate, which generates the stable
mineral magnesium carbonate (MgCO3). Key to process cost and viability are the carbonation reaction rate and degree of
completion. This process, which involves simultaneous dehydration and carbonation is very promising, but far from
optimized. Since Mg(OH)2 dehydration is intimately associated with
the carbonation process, its mechanisms are of direct interest in
understanding and optimizing the process. Although Mg(OH)2
dehydration has been extensively studied, relatively little is
known about the mechanism of the process, especially in the early
stages. Herein, we report on our investigation of the dehydration process using environmental-cell, dynamic
high-resolution transmission electron microscopy to directly observe the
process at the atom-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
nucleation and growth process occurring oxide layer formation.
These layers form lamellar oxycarbonate regions, which can grow both
parallel and perpendicular to the Mg(OH)2 lamella. The number of
oxide layers within the regions increases as they grow during
dehydration. Selected area diffraction suggests a novel
two-dimensional variant of Vegard law can describe the oxycarbonate
regions, with intralamellar Mg–Mg packing distances observed
between those known for MgCO3 and MgO. Intralamellar and
interlamellar elastic stress induced during dehydration 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. Mudala Dutta Bharadwaj, Ani Gupta,
Judith Yang, Unive. 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 epitelial 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 a metal oxide, we are visualizing the initial oxidation stage of
copper by in situ ultra-high vacuum (UHV) transmission electron
microscopy (TEM). Oxidation reactions for metallic systems are
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 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
reduces the rate of oxidation if both O2 and H2O are used.

SESSION Q10: INTERFACES IN METALS AND
CERAMICS II

Chair: Uli Fakhri and Joachim Mayer
Friday Morning, December 3, 1993
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. Millar, 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 a powerful tool,
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 beam TM and EELS to determine the local structure and to map the minoration across various boundaries. Polaron light microscopy plays an important role as well, not only in the characterization of boundaries but also in tracking segments of individual grains for the measurement of the strain. The essential role that each of these techniques plays in developing a better understanding of 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, Suzanne Steenwerck, Edward M. James, James P. Babcock, Kyoko Kawasaki, Julie A. Zborovska. University of Illinois at Chicago, Department of Physics, Chicago, IL; Gerhard Duscher, Vanderbilt University, Department of Physics, Nashville, TN; Myron M. Yacavone, Stephen D. Smolensky, National Institute of Standards and Technology 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 union 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 where analysis based on the known Schottky model 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) offers 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. Generally, most of the materials themselves have very varying compositions and are being developed to take advantage of different electronic properties. We have found that SrTiO$_3$, SrTi$_{1-x}$Mn$_x$O$_3$, (Ba,Sr)$_2$TiO$_4$, Y$_{2-x}$Bi$_x$O$_3$, Sr$_2$Ca$_3$Cu$_4$O$_8$, and Y$_2$Pb$_{0.5}$Sr$_{1.5}$Ti$_{0.5}$O$_3$ 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. Kevi T. Bachand, 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. CV, 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 in-situ, 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 our interest is in the behavior of ferro/piezoelectric domains and their interactions with the microstructure in PZT/PZN-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, microtomography 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 Hallman, 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 quench effects and defects from the ion-assisted deposition method employed, metastable alloys, nanostructured composite materials, nanolaminated heterostructures (superlattices), and amorphous-to-feltenike 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 fulleren-like domains. Here, sub-nanometer EELS chemical mapping and fine-structure analysis of elemental K-edge absorption edges will be reviewed. Results show that N is doped heterogeneously into a network of curved and interconnected graphic basal planes. For C-BN nanocubes grown in a solid matrix by reactive magnetron sputtering at low-T (350 C), an immiscibility between BN and C(N) was established. Also, CN and C bonding was observed for both structures and in the commonly observed BN and C-C. Thus, the magnetic/dielectric changes in 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. Superstructure structures can exhibit subcoherence strain. TEM and EELS experimental methods investigating 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. Generally, most of the materials themselves have very varying compositions and are being developed to take advantage of different electronic properties. We have found that SrTiO$_3$, SrTi$_{1-x}$Mn$_x$O$_3$, (Ba,Sr)$_2$TiO$_4$, Y$_{2-x}$Bi$_x$O$_3$, Sr$_2$Ca$_3$Cu$_4$O$_8$, and Y$_2$Pb$_{0.5}$Sr$_{1.5}$Ti$_{0.5}$O$_3$ 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.

11:00 AM Q10.5 INTERFACE ENGINEERING IN A COMBINED ARCHITECTURE WITH BALANCED MAGNETRON DEPOSITION SYSTEMS. GROWTH OF Ti$_{3}$AlC$_{2}$/Si FILMS ON STEEL. AN XTEM STUDY. L. Petros, R.D. Westen, Fredrick Seitz Materials Research Laboratory, University of Illinois, Urbana, IL, C. Schoenjahn, L.A. Dordue, 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 ions alters substrate surface chemistry, topography and microstructure, affecting subsequent film growth. This study compares Ti$_{3}$AlC$_{2}$/Si steel interfaces formed after metal ion bombardment at negative substrate biases, U$_{s}$, ranging from 600 to 1200 V during Cr cathodic arc, stabilized with a 0.06 Pa Ar background pressure. Samples pretreated with a 1200 V glow discharge at a pressure of 0.6 Pa were also investigated. Microstructure and microchemistry of the interfaces was studied by XTEM in-situ samples using STEM-EELS analysis. Cr ion doses of 1.2 x 10$^{13}$ ion/cm$^2$ 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 ~1.1μm. As U$_{s}$ was reduced to 600 V, the Cr-enriched layer grew into a 5 nm thick layer. Ar was incorporated at the surface to levels of 4 and 5 at.% during Cr sputtering and Ar glow discharge, respectively. Microstructure of Ti$_{3}$AlC$_{2}$/Si overlayers was dramatically affected by pre-treatment procedures. Ar sputter cleaned steel surfaces leading to a competitive columnar growth with small column size and open boundaries. In contrast, Cr irradiation at the same bias voltage results in local epitaxial growth of Ti$_{3}$AlC$_{2}$/Si overlayers, which is expected to improve film/substrate adhesion. Coatings deposited after Cr treatment with U$_{s}$ = 600 V 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 Diesley, Susan Simcott, Xudong Fan, Ma Yang, Department of Chemical and Materials Science, University of Kentucky, Lexington, KY.

Cougling high-resolution microscopy with atomistic simulations is an extremely powerful approach to understanding material- and interfacial phenomena in materials. Here we present complementary experimental and computational 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 28 and 368 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.

11:50 AM Q10.7
REAL TIME OBSERVATION OF GRAIN GROWTH IN SPATTERED Ag AND TiO₂ THIN FILMS. R. Dannenberg, BOC Coating Technology, Fairfield, CA; E.A. Such, 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 granules 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 increase, and plateaus at each succeeding temperature. Using a variant of the Mullins - Van 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 dewetting of the film from the substrate at 600°C. The dewetting failure is the high temperature limit of the thermal growing 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 TiO₂ 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. Kottul, J.J. Stephens, Sandia National Laboratories, Albuquerque, NM; Tan 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 aluminum, 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 aluminum-braze interface. A 100 x 75 pixel spectrum image was acquired from the aluminum-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 aluminum grains and glass sintering aid in the aluminum-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.