SYMPOSIUM FF
Materials Problem Solving with the Electron Microscope
April 17 – 19, 2001
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*Invited paper
SESSION FF1: THE FUTURE OF ELECTRON MICROSCOPY
Chair: J. Murray Gibson
Tuesday Morning, April 17, 2001
Salon 15 (Marriott)

8:30 AM *FF1.1
TEMS AND SYNCHROTRONS: STRENGTHS AND WEAKNESSES
John Spencer, Dept. of Physics, Arizona State University, Tempe, AZ.

X-ray and electron beams interact differently with solids, yielding different kinds of information. This talk compares the instrumental factors (brightness, coherence, detectors, lenses, stages), the interactions (charge, spin, potential, radiation damage) for each, and provides case studies. For the highly coherent beams now available from both synchrotrons and field-emission TEM/STEM, we give comparable examples of diffraction, imaging, spectroscopy and magnetization imaging, both probe. Each will include the study of diffuse scattering by both methods, X-ray and HREM imaging and holography, absorption spectroscopy (ELS, ELNES, EXAFS) in the soft-X-ray region, standing wave fluorescence experiments by both methods, magnetic diffraction and holography and crystallographic problems with organic materials.

9:00 AM *FF1.2
IMPROVEMENT OF IMAGING INTERFACES BY MEANS OF A SPHERICAL ABERRATION-CORRECTED 200 KV TEM
Max Haider, CEOS GmbH, Heidelberg, GERMANY.

Rose[1] proposed in 1998 a hexapole corrector with which the point resolution could be improved the first time by correcting only the spherical aberration. This corrector is based on two electromagnetic hexapoles and four additional lenses[2]. The basic instrument was a standard 300 kV TEM equipped with field emission gun. With this modified microscope we were able to demonstrate the correction of the spherical aberration, the availability of an automated alignment routine[3] and to realize an improvement of the point resolution from 0.24 nm to better than 0.14 nm[4]. In the case of a Cs corrected TEM this spherical aberration coefficient becomes a free tunable parameter. However, the damping of the contrast at high spatial frequencies due to the temporal coherence of the electron emitter limits the attainable information limit. The compensation of the chromatic aberration for a TEM by means of a corrector is not yet feasible but the energy spread of the gun can be reduced by the incorporation of a monochromator and, hence, a point resolution below 1.8 nm can be achieved by an accelerating voltage of U = 200 kV. In the case of a 300 kV TEM and an energy width of δE < 0.2 eV a point resolution closer to 0.5 nm can be approached. The main advantage of spherical aberration correction is the structure-independent artifacts due to contrast delocalization can be avoided to a great extent[5]. These artifacts have turned out to be a major obstacle for the application of STEM instruments to defect and interface studies. Contrast delocalization arises from the width of the aberration disc belonging to the individual diffracted electron waves whose diameter increases with Cs. The application of this corrected TEM have been carried out in the group of K. Urban at the Research Center Juelich.


9:30 AM *FF1.3
ABERRATION-CORRECTED STEM
N. Delby, O.L. Krivinec and P.D. Nellist Nion, R&D Dept, Kirkland, WA.

Scanning transmission electron microscopes (STEMs) have several major advantages over conventional (bright-field) electron microscopy (CTEMs): 1) they work best in the incoherent high-angle dark field (HADF) imaging mode, which gives 400% better resolution than the phase contrast mode typically employed with CTEMs, 2) they allow spatially-resolved data and even images to be obtained from any signal including electron energy-loss and X-rays, and thus readily provide information about the composition and chemical properties of the sample, 3) they are less sensitive to the effect of chromatic aberration, and 4) their optical simplicity is simpler because they only have to focus the electrons into one narrow beam rather than into an image of a sample. In the absence of an objective aperture, typical Cs limits of 0.3 nm for STEMS is typically due to the spherical aberration of their objective lens. A spherical aberration (Cs-) corrector allows C, to be set to a very small value (typically a few tens of microns) that best corrects Cs. This can have a large effect of higher order aberrations such as C4. It typically allows the resolution to be nearly doubled and the beam current to be increased by about a factor of 10.

We have built such a corrector and made it available commercially. In this paper we will discuss the practical experience gained from using C,-corrected STEMs to image and analyze real-world samples, and point out the directions aberration-corrected STEM is to take in the future. Among other conclusions, we will show that a C,- corrector places severe demands on the rest of the microscope column, and we will discuss the ways to meet these demands.

10:30 AM *FF1.4
ADVANCED TEM INSTRUMENTATION FOR INTERFACE STUDIES
Manfred Ribbe and Wilfried Sigle, MPI für Metallforschung, Stuttgart, GERMANY.

It is of great importance and interest to investigate the structure, composition, and bonding of interfaces existing in materials. Since these investigations require quite close to the interfaces it is important to carry out the investigations with high spatial resolution: the atomic structure of specific (tilt) interfaces can be determined by high-resolution transmission electron microscopy in the field emission gun (HRTEM), analytical electron microscopy (AEM) generates information on the composition of information. Those AEM studies include energy dispersive X-ray spectroscopy as well as electron energy-loss spectroscopy. From the energy-loss near-edge structure (ELNES) of ionization edges information on the local electronic structure at interfaces can be obtained. It should be possible to also extract information on bonding from those ELNES structures. Presently a new instrument is being developed for our institute, which combines the different capabilities of analytical instruments in a single TEM/STEM: the SESAM (Sub-V-Abs Angstrom Microscope) built by LEOS and CEOS. The instrument will be equipped with a field emission gun (Schottky type, 200 kV) and a monochromator (CEOS) which can reduce the energy spread of the electrons to 0.2 eV. A MANDOLINE energy filter will be installed allowing for a much higher transmission as compared to conventional Omega filters or Gun Imaging filters.

11:00 AM *FF1.5
APPLICATION OF SPHERICAL-ABERRATION-CORRECTED TRANSMISSION ELECTRON MICROSCOPY TO MATERIALS SCIENCE

Recently it has been demonstrated that it is possible to correct the spherical aberration of the objective lens of a 200 kV transmission electron microscope equipped with a field emission gun by application of a double-hexapole element [1]. The prototype instrument, a Philips CM200 with a superwin lens exhibits a point resolution close to the information limit of about 0.135 nm using the standard double-tik stage with ±40° tilting angle. Application of this instrument for cluster, defect and interface studies shows that besides the gain in resolution the prominent advantage of spherical aberration correction is the reduction of contrast delocalization. The result is a unique quality of high-resolution images of defects and interfaces. Depending on the (adjustable) value of the spherical-aberration coefficient C, the contrast for high resolution can be selected with respect to phase-contrast (C > 0) and amplitude-contrast (C = 0) contributions. Other advantages for materials problems solving arise from improved Bragg-diffraction dark-field and selected area diffraction properties. Examples of the application of the instrument to structure studies in electroceramic perovskite materials, Si/Al-films and compound semiconductor heterostructures will be presented.


11:30 AM *FF1.6
ABERRATION-CORRECTED MICROSCOPE DESIGN FOR LARGE-GAP IN-SITU ELECTRON MICROSCOPY
Kai Xing, Univ of Illinois at U-C, Dept. of Physics, Urbana, IL; J. Murray Gibson, Argonne National Lab, Materials Science Div, Argonne, IL

There is a scientific interest in developing high performance transmission electron microscope with large objective lens gaps to permit in-situ experiments. Using current designs for spherical aberration (Cs) correction[2], we will discuss the advantage of high performance performance available as a function of gap size. Calculations include realistic lens configurations and the effect of instabilities and stray fields. The ultimate performance can be achieved only by correcting both Cs and chromatic aberration (Cc). We have theoretically analyzed several configurations to achieve this, including quadrupole-octopole corrector and hybrid hexapole-quadrupole octopole corrector. Analysis includes consideration of aberrations, fifth-order axial aberrations and use for STEM and for TEM.

References:
VOLUMETRIC CHARACTERISTICS OF NONSTRUCTURED POLYMER SYSTEMS BY TRANSMISSION ELECTRON MICROSCOPY. Richard Sponza, North Carolina State Univ, Dept of Chemical Engineering and M&E, Raleigh, NC; Hiroshi Jinmi, Kyoto Inst of Technology, Dept of Polymer Science & Engineering, Kyoto, JAPAN; David Agerd, Univ of California, Dept of Biochemistry & Biophysics, San Francisco, CA.

Nanostructured polymer systems are of tremendous technological and fundamental interest due to their potentially complex morphologies and multifunctional properties. While transmission electron microscopy continues to provide valuable structural information concerning such systems, their volumetric characteristics remain elusive. In this work, we demonstrate how transmission electron microscopy (TEM) can be used to investigate such nanostructures and directly measure features including, but not limited to, interfacial curvature, interfacial area, and interjunction distances. In this work, we first present the principles of the filtered back-projection reconstruction algorithm and then apply this approach to a variety of diverse examples. Bicontinuous block copolymer nanostructures, such as the gyroid and sponge, will be discussed in detail, and their characteristics will be quantitatively compared to models and other bicontinuous polymer nanostructures that exist at larger length scales. A new tricomponent block copolymer nanostructure formed by a microphase-ordered ABC triblock copolymer will be presented, as will results from non-equilibrium body-centered cubic structures as they strive to reach equilibrium as cylinders upon crossing the sphere-to-cylinder order-order transition. The in-situ morphology of bicontinuous polymer latex particles generated in supercritical CO2 will also be addressed here through the use of TEM.


Fluctuation microscopy is a recently-developed transmission electron microscopy technique that is capable of detecting and characterizing medium range order in disordered materials. The technique, as implemented by the authors, examines the speckle in hollow cone dark field images of thin dispersed materials, as a function of hollow cone angle. This method is also called variable coherence microscopy. The speckle is an image that is measured by computing the variance of the image intensity. Any strong peaks in the variance versus hollow cone-angle plot is a signature of order. Image simulations indicate that a true continuous random network should show very little structure in the variance plots. In this talk, I will outline the theory of fluctuation microscopy, explaining why it works when simple diffraction fails. I will also present experimental and simulation observations of medium range order in amorphous silicon and germanium films.


In many systems, small volumes of amorphous or polycrystalline material play a crucial role in determining materials properties. This is increasingly the case as the dimension of structures decreases towards the nanoscale. The technique of RDF analysis is a powerful tool for characterizing these materials. It is used to determine the relative contributions of amorphous materials. In this work, we use the technique of RDF analysis to determine the relative contributions of amorphous materials. In this work, we use the technique of RDF analysis to determine the relative contributions of amorphous materials. In this work, we use the technique of RDF analysis to determine the relative contributions of amorphous materials. In this work, we use the technique of RDF analysis to determine the relative contributions of amorphous materials. In this work, we use the technique of RDF analysis to determine the relative contributions of amorphous materials.

COSTS OF NUCLEATION AND MIGRATION OF NANOCRYSTALS. M. Shoemaker, UCSD, San Diego, CA; J. C. Baker, UCSD, San Diego, CA; J. C. Lee, UCSD, San Diego, CA.

Nanocrystal nucleation and growth are processes that can significantly affect the properties of nanomaterials. In this work, we investigate the costs of nucleation and migration of nanocrystals. We use a classical nucleation theory approach to calculate the free energy of nucleation, which is given by the product of the surface energy and the number of particles in the nucleus. We also consider the cost of migration, which is given by the product of the migration energy and the number of particles that must move to the nucleus.
level, both within the coating and at the coating-substrate interface. Using multivariate statistical analysis it is hoped to separate and quantify the contributions to the energy spectra from the TiC, grains and the amorphous matrix in the high-carbon material.

Electrochemically prepared Si nanoparticles display extremely strong luminescence even though bulk Si is an indirect band gap semiconductor. This property is undoubtedly due to the high surface-to-volume ratio of these small particles. Our ab-initio calculations suggest these particles possess 'magic numbers' of atoms with exceptionally high stability; the smallest of these is a 29 atom Si cluster. Calculations show the surface atoms are dimerized to reduce the total energy and enhance the stability of the cluster. This dimerization may also account for their strong luminescence by breaking the local inversion symmetry allowing second harmonic generation. In order to verify the results of the ab-initio calculations, we are investigating this system using electron diffraction. Comparing simulated diffracted intensities of relaxed and unreleased 'magic number' clusters, we have found clear differences in the diffuse scatter between Bragg positions. These differences can then be used to fingerprint experimental diffraction patterns and to refine the atomic positions of the atoms in the clusters. We have obtained diffraction patterns from individual clusters using sub-micrometer electron probes. These patterns demonstrate the effectiveness of this technique. Unfortunately, the low signal-to-background of the patterns precludes the examination of the diffuse scatter owing to the scintillating nature of the carbon support film. We are currently developing simulation and experimental investigations of the diffraction from these particles to determine the feasibility of this method, and pursuing additional sample preparation methods to reduce the effect of the support film. Work at the Center for Microanalysis of Materials is supported by the US DoE under grant DEFG02-98ER45439.

4:30 PM FF2.8 THE EFFECT OF VANADIUM ADDITION ON MICROSTRUCTURES OF ULTRAFINE GRAINED LOW CARBON STEEL MANUFACTURED BY ECA PRESSING. Sangmin Kim, Jongryul Kim, Donghyun Shim, Hanyoung Univ, Dept of Metallurgy and Materials Engineering, Amsan, Kyungsri-Do, KOREA (SOUTH).

Ultral fine-grained (UFG) low carbon steels manufactured by ECP demonstrated excellent mechanical properties, especially high yield strength. For practical applications, the UFG steels possess low yield ratio due to the extensive plastic deformation accumulates extensive internal energy inside material, which requires heat treatment for the relief of residual stress. However, it is difficult to control the grain size during heat treatment owing to that the structural instability results in abnormal grain growth. In order to take full advantages of the UFG steels, this investigation is aimed to maintain the grain size below a submicrometer scale after heat treatment by the addition of vanadium. SEM and XRD have been used to investigate the microstructural evolution of the steels with different vanadium contents during ECP. According to results, the effects of vanadium additions on the microstructure of the steels produced by ECP are as follows: 1) Iron carbides, which existed in perlite, were observed to be evenly distributed the whole ferrite boundaries of a sample after ECP, whereas they were found in the vicinity of perlite without vanadium. 2) Coherent vanadium precipitates were nucleated heterogeneously as dislocations inside grains. 3) The mean particle size of the precipitates increased with increasing contents. 4) There existed the effective size of vanadium carbides for dislocation pinning and grain growth inhibition. These results clearly indicate that the vanadium precipitate recrystallization behavior (especially in 1), this phenomenon would be related to the dissolution and re-precipitation of carbon, which might strongly affect the recrystallization. Until now, we have obtained the mean grain size of ~3 μm and ~7% yield ratio by adding vanadium which nearly satisfy the practical guideline. For the further improvement, the conditions of heat treatment and the role and mechanism of iron precipitations are under investigation using HRTEM and TEM.
nanocharacterization of materials using a full array of modern analytical techniques including electron microscopy, scanning probe microscopy, analytical techniques, and various spectroscopies. The CMM places strong emphasis on in-situ material science and has developed several unique instruments permitting dynamic studies in surface, interface, and thin film science under ultrahigh vacuum and as in aggressive environments. The CMM is a facility for collaborative research and education in the effective use of modern nanocharacterization techniques. A distinctive feature in CMM mode of operation is that the staff works directly with users to modify the instruments and develop new techniques, in order to create new capabilities and obtain new knowledge. A subset of these unique instruments include: an environmental-cell TEM with high and low temperature stages, an UHV high-temperature (≤ 1800K) LEEM with MBE facilities, a 2k Tesla STM, and a UHV STM with in-situ deposition, ion-irradiation, and gas-doping, an in-situ film growth imaging XPS, and cryogenic temperature/high magnetic field XRD. Here, we will highlight materials problems solved enabled by the CMM. Contributions will include growth of high mobility GaAs and In GaAs quantum wells on GaAs substrates and surface crystallography, nano-photography and evolution, and surface diffusion kinetics in heterogeneous refractory metal and refractory transition-metal nitrides, structure and reactivity relationships of diamond heteroepitaxial films and the interaction of hydrogen and the dislocations. The Center for Microanalysis of Materials is supported by the US DOE under grant DEFG02-98ER45439.

FF4.3 EXPLATING THE FIRST RETREATS OF MICROANALYSIS: RESEARCH FACILITY DEVELOPMENT AT THE ELECTRON MICROSCOPE CENTER AT ARGONNE NATIONAL LABORATORY. Dean J. Miller, The Electron Microscope Center, Materials Science Division, Argonne National Laboratory, Argonne, IL.

The Electron Microscope Center at Argonne National Laboratory maintains a leading international role in research on in situ studies of transformations and defect processes, ion beam modification, and ion irradiation effects, superconductors, ferroelectrics and interfaces. Its high and intermediate voltage electron microscopes coupled with a Tandem accelerator represent the only such system in the US. The EMC also has resident expertise in instrumentation design, microcharacterization technique development and telepresence collaboration. Together with the other DOE-supported user facilities, the EMC helps to develop and expand the frontiers of microanalysis by fostering the sharing of jointly held resources in instrumentation, techniques and scientific expertise. In this paper, an overview of the facilities, operation and access procedures, and selected research highlights will be presented.

SESSION FF4: POSTER SESSION
Chair: Mark Newhall
Tuesday Evening, April 17, 2001
8:00 PM
Salon 1-7 (Merritt)

FF4.1 EFFECTS OF ELASTIC WAVES ON ANNULAR DARB-FIELD STEM IMAGE. Krastan Nikolaite, Marsha Takedachi, Hidehiro Yamauchi and Kunio Furuya National Research Institute for Metals, Tsukuba, JAPAN.

Since the image of isolated heavy atoms was obtained using a scanning transmission electron microscope (STEM) equipped with annular detector, the method has been developed at a constant pace, and electron probes of atomic dimensions have become available. By using a high-angle, wide range annular detector, the image is mainly formed from thermal diffuse scattering (TDS) electrons, and the coherent contribution of the image is averaged to be an incoherent image with a strong contrast between electrons of different energy. Therefore, the images obtained from STEM are expected to be intuitively interpreted with no contrast reversal along with the defocus and/or specimen thickness changes, in contrast with phase contrast images from HTEM. However, the image made from coherent electron still shows the coherent nature in some situations. Those conditions on various cases were studied extensively by many authors, and it was revealed that the incoherency of the image may not be achieved in some cases and strongly excited diffused beams and/or channeling of probe electron may play an important role in the image. Therefore, the appropriate selection of parameters, such as defocus and detector angles, are essential in STEM imaging. It means that the image obtained from STEM is still needed in order to achieve the appropriate coherent imaging condition. Recently, many trial to measure the contrast sensitivity and/or positions from slight intensity difference of STEM is being performed, so that demand for the accurate and fast simulation method is increasing, and those theoretical analyses are studied by several authors. Recently, authors proposed new scheme calculating, which can estimating simultaneous diffused beam intensities together with TDS intensities. Using this method, the features and affect of elastically deflected waves in ADF-STEM image is discussed in comparison with multislice based method for various calculation parameters.

FF4.2 REAL-TIME ELEMENTAL MAPPING OF SEMICONDUCTOR DEVICES. Kazunori Kaji, Takeshi.Asano, Hitachi Research Laboratory, Hitachi Ltd., Bunkyo, JAPAN; Shunroku Tago, Hirohiko Tanaka, Shigeo Ishizawa, Instruments Group, Hitachi Ltd., Bunkyo, JAPAN.

A new type of elemental mapping system which consists of a two-window energy filter and an scanning transmission microscope has been developed. The energy filter has two kinds of electron beam detectors. One is a duality detecting unit for observing each element maps and the other is a parallel detection system for measuring electron energy loss spectra. Mapping images are obtained by real-time division of two signals from the dual detector unit. Clear oxygen and nitrogen maps in cross-sections of a semiconductor or device can be obtained with spatial resolution of 1 nm. In this system a detecting element can be switched to another one while scanning the electron beam on the specimen so that the boundary of two elements can be determined with nanometer resolution.

FF4.3 INVESTIGATION OF SELF-ASSEMBLED INP QUANTUM ISLANDS BY TRANSMISSION ELECTRON MICROSCOPY. Angelo Fantini, Fritz Philipp, Max-Planck-Institut fuer Metallforschung, Stuttgart, GERMANY, Joerg Porsche, Ferdinand Scholz, 4 Physikalisches Institut, Universitat Stuttgart, GERMANY.

Transmission electron microscopy (TEM) studies of self-assembled InP quantum dots for injection lasers with an optical emission in the red part of the spectrum have been performed in this work. The samples were grown by low pressure metal organic vapor phase epitaxy (MOVPE) on [001] GaAs substrates with different orientation angles toward the [111] a-plane using the Stranki-Kastner growth mode. Choosing appropriate growth parameters, the deposition of 3.4 monolayers InP on GaAs leads to the nucleation of coherently strained, small quantum islands due to the miscut of 3.7°. Investigating the vertical stacking behavior of three- and stacks of InP quantum dots, has led us to introduce a correlation function which describes the correlation of island position alignment between two InP layers and the next. The course of maximum of the correlation angle distribution is a function of GaInP spacer layer thickness, degree of substrate misorientation and growth temperature has been determined. Cross-sectional TEM samples were prepared using standard methods. We studied island morphology by using conventional diffraction contrast (bright-field / dark-field) imaging in a Philips CM 200 microscope in two beam diffraction conditions. HREM investigations were carried out on a JOEL 4000EX microscope accelerating at 400 KV to study the strain field of quantum dots between adjacent InP layers. Ordered domains and their boundaries are investigated in dark-field modes. We found an increasing correlation-angle for quantum dots with decreasing spacer thickness. The alignment of the InP dots occur in opposite direction to the misorientation of the substrate and domain boundaries. HREM images are directly confirming such behavior.


Compositional graded AlGaAs layers are important material for graded-index waveguide applications, wherein the index of refraction varies continuously with Al content. Successful application of these materials requires characterization techniques that can accurately quantify both, the shape of the graded profile and its composition. The use of techniques such as secondary ion mass spectrometry (SIMS) and Auger electron spectroscopy (AES) pose problems due to insufficient spatial resolution and inaccuracies in composition due to smearing from adjacent layers. In this study we employ the X-ray energy dispersive spectrometry technique to characterize a variety of AlGaAs layers with linear, parabolic and sinusoidal grading in the Al content. The individual layers were grown by molecular beam epitaxy and the Al composition monitored in-situ by spectrosopic ellipsometry (SE). The XEDS measurements were obtained using a field emission gun transmission electron microscope (FEG TEM), to exploit the small probe size (high spatial resolution) and high brightness (improved sensitivity) associated with the FEG source. The Al/Ga composition...
profiles were determined based on the CH3Lorimer (CL) equations, assuming the thin-film criterion. The so-called k-factors in the CL equations ($k_{1-A}$, $k_{2-A}$, and $k_{1-2}$), required for calculating the composition profiles, were determined from pre-calibrated AlGaN$_{2-x}$As layers. Further details on the comparison between XEDS results with those obtained from SIMS, AES, and the SE will be presented in a subsequent discussion. This fixed film-growth related problems, such as flux transients, will also be discussed.

**FP4.5**

**TEM STUDIES ON CO$_3$S$_2$ AND Ni$_3$S$_2$ FORMATION.** J. Falk, S. Teichert, H. Giesler, B. Gebhardt, G. Beddar, H.-J. Himmelberg, Inst. of Physics, Tech Univ Chemnitz, Chemnitz, GERMANY.

Co$_3$S$_2$ and Ni$_3$S$_2$ are stable silicides with Co$_2$S$_3$ structure and lattice constants close to that of Si. Difficulties in providing the C54 phase of Ti$_2$Si$_2$ in submicron structures led to a new interest in the Co/Si and Ni/Si systems. Investigations by means of electron microscopy are necessary for understanding growth mechanisms of these systems on a nanoscale. We will present some results of detailed TEM studies in this field partly related to RBS and electrical measurements. The Co$_3$S$_2$ growth by solid phase reaction of Co films with Si$_2$N$_2$C$_2$ (001) substrates ($x = 0.0, 0.001$ and $0.005$) and of Co/Th and Co/Hf/Si$_3$N$_4$ with Si(001) substrates in N$_2$ atmosphere was investigated. TEM on the Co/Si$_2$N$_2$C$_2$ system after thermal treatment revealed an increased appearance of a few preferred orientation relations between CoSi$_2$ crystallites and the substrate with rising carbon content $x$. Especially the amount of the epitaxial A-type and the twinned at the (111) planes B-type increased notably. RBS and electrical measurements showed a shift of the Co$_2$Si to Co$_3$S$_2$ transformation temperature to higher values with rising $x$. TEM investigations on the Co$_3$S$_2$ growth on pure Si using Ti or Hf as diffusion barrier forming metals showed that, the formation of epitaxial Co$_2$S$_2$ films proceeds through an intermediate textured Co$_3$S$_2$ phase. The epitaxial Co$_2$S$_2$ was found to nucleate at the Co/Si interface with a more pronounced delay compared to that observed in the Co$_2$Si$_2$C$_2$ system. The ternary top layers remaining after the solid phase reaction of the bimetallic Si with Co were etched in a CF$_3$/Ar plasma. Co$_2$S$_2$ identified with the help of the Co edge in EELS spectra was found to be of importance during the etch process of Co$_2$S$_2$. Furthermore self-assemblying of Ni$_3$S$_2$ precipitates in a Si(001) matrix was studied and discussed in reference to the formation of Ni$_3$S$_2$ and Ni$_2$Si$_3$ codeposition in a MBE system a variant of the self-assembly behavior of the Ni$_3$S$_2$precipitates was observed.

**FP4.6**

**IN SITU INVESTIGATION OF THE FORMATION OF NICKEL SILICIDES DURING INTERACTION OF SILICON WITH NICKEL.** Boris Boldyrev, Mikhail Korotkin, Institute of Solid State Chemistry, Siberian Branch, Russian Academy of Sciences, RUSSIAN FEDERATION.

In situ investigations showed the next sequence of phase formation during interaction of nickel particles with single crystal (100) and amorphous silicon: a) within the temperature range till 500 C, the first and prevailing phase formed is Ni$_5$Si$_3$, b) annealing at temperatures above 600 C is accompanied by the formation and epitaxial growth of Ni$_3$Si$_2$ phase. The growth of nickel disilicide crystal phase is accompanied by the formation of both the NC and Ni$_3$Si$_2$ at the nickel disilicide phase, and in phase Si$_2$. The interaction of the amorphous silicon film with nickel particles at temperatures above 600 C leads to the formation of nickel silicides: Ni$_5$Si$_3$, Ni$_3$Si$_2$, Ni$_2$Si$_3$. The formation of silicide phases in the interaction of nickel particles with silicon during annealing did not confirm the formation of intermediate amorphous silicide that was observed earlier in thin-film metal-silicon systems. The irradiation with the beam of accelerated electrons in microscopy leads to the increase of the rate of silicide phase formation and to the decrease of the temperature, at which nickel silicide phase growing epitaxially is formed, is, at least, to 400 C. In our case, we observed a decrease of the growth rate due to the radiation defects in the structure of single crystal silicon.

**FP4.7**

**CHARACTERIZATION OF OXYGEN-DOPED V$_4$[Cr$_2$O$_8$] ALLOYS.** J. Bentley and B.A. Pint, Oak Ridge National Laboratory, Metals and Ceramics Division, Oak Ridge, TN.

With their consideration as structural materials in proposed fusion reactors, V$_4$[Cr$_2$O$_8$] alloys have been the subject of a significant research effort for more than five years. One aspect of this work is the sensitivity of mechanical behavior to oxygen content, this being of special importance to weldments. Following a 1-b-melt at 1200C, sheet specimens were subjected to anodizing (16h to 48h) 500C anneals in 5 to 8 x 10$^{-6}$ torr oxygen, followed by a homogenization vacuum anneal of 100 h at 600C. Weight gains indicated ~2000 to ~10000 ppm oxygen during aging. Microcracks by transmission electron microscopy (TEM) were performed for correlation with tensile data. Techniques included diffraction contrast analyses of secondary defects, energy-filtered transmission electron microscopy (EFTEM) imaging, and high angle annular darkfield scanning electron microscopy (EDS) with focused probes. Following oxygen doping and homogenization, high concentrations of nanoscale clusters on (001) were observed in the matrix with a 25nm-wide precipitate-free zone (PFZ). This corresponds to a depletion in Ti level, apparently arising from a collector-pluton mechanism for the formation of Ti$_2$(C,CN) intergranular precipitates. These precipitates give a wide variation in size and concentration from boundary to boundary. Additional vacuum anneals for 4h at 950C resulted in the formation of coarse typically 1-3nm diameter plate precipitates <5nm thick, again on (001). The detailed microstructural characterization results will be presented to summarize to mechanical properties. Research supported by the Office of Fusion Energy Sciences and at the ORNL Shared User Facility by the Division of Materials Science and Engineering, U.S. Department of Energy, under contract DE-AC05-840R22725 with UT-Battelle, LLC.

**FP4.8**

**MICROSTRUCTURAL ANALYSIS OF ULTRAFINE GRAINED MATERIALS PRODUCED BY ECAP.** Inyoung Kim, Jonggoyl Kim, Dong Hyuk Shin, Hanyong Unv, Dept of Metallurgy and Materials Engineering, Ansan, Kyungsung, KOREA (SOUTH).
the CuNiBe alloy shows that both continuous and discontinuous precipitation occur in this alloy. Large lamellar discontinuous precipitation zones adjacent to grain boundaries show significant effect on the fracture behavior of this alloy. The strain localization in discontinuous precipitation zone adjacent to grain boundaries results in grain boundary ductile fracture at room temperature. As temperature increases, both the strength of copper matrix and the strength of grain boundaries decrease, and they are assumed to be responsible for increased percentage of intergranular fracture, and the reduction of overall fracture resistance as elevated temperatures.

**FF4.11 TEM AND LVSEM INVESTIGATIONS FOR THE CHARACTERIZATION OF COMPACTIONIZED POLYMERIC HYBRID INTEGRATED CIRCUITS.** Thorsten Spich, Jürgen Petermann, University of Dortmund, Dept of Chemical Engineering, Dortmund, GERMANY.

Laminated polymer films have become of technical importance due to their advantages in a broad scope of applications. In the majority of cases, they contain layers of insulating polymers, the system polyethylene/polypropylene being one of the most common used. As an addition between these non-pole polymers is rather weak, compatibilizers have to be used to increase the strength of adhesive bonding. Usually, the weak interfacial adherence of two insulating polymers A and B is strengthened by adding an interdiffusing block copolymer A-B. In this work, an alternative approach was performed by using an interface layer of a fine dispersed blend A/B which was expected to cause adhesion by mechanical interlocking. To determine the strength at the interface points, a modified T-peel test was applied, allowing to measure detachment forces for the untreated as well as for the compatibilized interface within the same sample. To obtain information on the interfaces, multi layer stackings comprising films of PE and PP, adhering with layers of compatibilizer, were prepared. Cross-sectional micromot cuts of these stackings were taken and examined by LVSEM. Low voltage technology enabled us to obtain a topographic image of the polymers without surface coating. For TEM investigations, two-step replicas of the smooth and etched sample surfaces were prepared, reveiving insulating techniques in PE as well as in PP. Both kinds of electron microscopy turned out to be excellent means for the examination of the melt crystallized interface morphologies, allowing to determine the parameters which significantly influence the compatibilizers' adhesion properties.

Mechanical interlocking in µm-scale was clearly illustrated. Additional information on the mechanisms of bonding was obtained by directly examining the peeled surfaces of the laminated films in the LVSEM.

**FF4.12 ELECTRON MICROSCOPY APPLICATION ON THE STUDY OF A PHASE SEPARATION PHENOMENON IN AN ACRYLIC SYSTEM.** R. Velázquez, J. Reyes and V. M. Castro, Instituto de Física, UNAM, Líbreratario de Juriquila, Queretaro, MEXICO.

An acrylic system consisting of methyl methacrylate and triethylenglycol dimethacrylate undergoes phase separation when the system is synthesized through bulk polymerization using N, N dimethyl p-toluidine as an initiator. The separation produces the formation of microdomains with different chemical compositions. The size, shape and morphology of these microdomains have a strong influence on the final mechanical properties of the polymers; therefore, good observations of these microdomains were basic in this research. In order to do the electron microscopy observations, it was necessary to improve a new sample preparation technique, which employs a solvent mixture of acetone and chloroform to make a selective chemical attack on the interface between the microdomains. The solvent mixture was put in contact to the polymer during one hour, using agitation by an ultrasonic device. This technique is similar to that technique use in metals to observe grain boundaries. The application of this new technique suggest the scanning electron microscopy observations and it was possible the study of the phase separation mechanism and the study of the influence of the formulation of the polymer on the morphology and microstructure of the domains. Results from Differential scanning calorimetry, Infrared and MicroRaman spectroscopies complete the microstructural characterization of the microdomains.

**FF4.13 ELECTRON BEAM INDUCED EFFECTS IN METAL-MORPHOUS CHALCOGENIDE FILMS.** Katrin Mietusch, Alexander G. Fitzgerald, Nurmiah, Mervin J. Rose, University of Dundee, Dept of Electronic Engineering and Physics, Dundee, SCOTLAND.

Amorphous chalcoptides in contact with silver or copper exhibit a remarkable sensitive forms of degradation. In this study the influence of electron beam irradiation on bi-layers of amorphous chalcoptides and silver or copper has been investigated. A focused electron beam was utilized to produce patterns of nanometer dimensions, such as fine lines, dots, holes and patterns in these films. The scanning electron microscopy, Auger electron spectroscopy and atomic force microscopy have been employed in this study. A variety of parameters influence the growth characteristics and properties of these patterns. Important parameters include, as the film thickness and the metal content affect the sensitivity of the bi-layers to electron irradiation. The size of the patterns could be controlled by optimising the exposure conditions, such as accelerating voltage and beam spot size. Auger electron spectroscopy revealed that the lines had a metal content than the remainder of the films. In addition, the conductivity of linear patterns has been investigated.

**SESSION FF5 ELECTRONIC AND SEMICONDUCTING MATERIALS.** Chair: Eric A. Stoch, Wednesday, April 18, 2001

**FF5.1 ACCURACY OF HRTEM GATE OXIDE THICKNESS MEASUREMENTS.** John Henry Scott and David S. Bright, NIST, Surface and Microanalysis Science Division, Gaithersburg, MD.

The accuracy of high-resolution TEM gate oxide thickness microscopy is studied using multilayer simulations of HRTEM micrographs. Computer models of ultrathin amorphous silicon dioxide films, situated between two crystalline silicon layers are used to produce simulated HRTEM images of the stack in cross-section. Gate oxide film thickness measurements are obtained from the simulated micrographs using the same image processing techniques used for equivalent experimental micrographs. The resulting thicknesses are compared to those derived from the oxide thicknesses in the model, thus determining the accuracy of individual measurements. The efficacy of different image processing and measurement methods are compared, and the effects of variations in imaging conditions such as beam voltage, beam tilt, defocus, along-beam thickness, magnification, and sample vibration are studied systematically.

**FF5.2 NANOSCALE STUDIES OF STRESS DISTRIBUTIONS, DEFECTS AND MICROSTRUCTURAL DEGRADATION MODES IN SEMICONDUCTOR DEVICES.** R. Hall, J. Demarest and D. Mathes, Department of Materials Science, University of Virginia, VA, K. Schonenberg, BMI, East Fallow, NY, K.D. Choquette, Electrical Engineering Department, U. Illinois, IL, K.M. Geib, Sandia National Laboratories.

We show how the combination of focused ion beam (FIB) specimen preparation, quantitative electron diffraction contrast analysis, and application of in-situ thermal, electrical and optical stresses in the transmission electron microscope (TEM) provides new means for nanoscale analysis of stress distributions, defect generation and degradation modes in semiconductor devices. The application of FIB sputtering and deposition to TEM specimen preparation is becoming an increasingly important technique in nanostructural analysis. One prominent advantage of FIB specimen preparation is that it produces thin membranes of uniform and defined geometry. This enables accurate application of the Howie-Whelan equations to correlate electron diffraction contrast intensity maps to local stress distributions. Applications to stress mapping in semiconductor device structures with spatial resolution of order 10 nm and stress sensitivity of order 30 MPa will be presented. The FIB is also an extremely powerful tool in enabling in-situ application of a wide range of signals in the TEM. We have successfully combined FIB micro-machining and micro-contacting techniques to enable in-situ application of electrical and optical signals to sectioned (membrane thicknesses in the hundreds of nm range) laser diode structures in the TEM. Materials degradation modes as functions of applied in-situ thermal, electrical and optical stresses are compared to those observed in un-sectioned degraded structures. The characteristics degradation modes associated with ‘bulk’ devices that are intentionally degraded include threading dislocations that extend throughout the device structure and which are apparently associated with the current confinement structures used in these laser devices. Further, these threading dislocations nucleate additional dislocation loops within the optically active region. Preliminary in-situ experiments demonstrate dislocation generation rates that are dependent upon electrical current density.

**FF5.3 MEASUREMENT OF LOCAL STRAIN IN THIN ALUMINIUM INTERCONNECTS USING CONVERGENT BEAM ELECTRON DIFFRACTION.** Stephan Kramer, Cynthia A. Volkert, Eduard Arzt, Manfred Röhle, MaxPlanck-Institut für Metallforschung, Stuttgart.
Energy filtered convergent beam electron diffraction (CBED) was used to measure lattice parameters with high spatial resolution (10-180 nm) in unpassivated aluminum interconnects with widths smaller than 1 μm. The transform of the CBED patterns was computed in the detection of the higher order Lz line (HOLZ) line positions and by treating dynamical diffraction effects separately for each individual HOLZ line, it is possible to improve the accuracy of the quantitative analysis. An additional strain state can be routinely evaluated with an accuracy of 10^-4. Measurements were performed as a function of position along the interconnect in both thermally-cycled and electromigrated samples. The strain state is predominantly uniaxial and the details agree well with predictions of elastic finite element modeling. However, the strain state varies locally within single grains, as well as from grain to grain, in both types of samples by as much as 50%. This cannot be explained by elastic or plastic micromechanics. This study demonstrates the potential for orienting single crystalline grains by localized heating and thus their mechanical properties and power handling capabilities. In this study, we examine the formation of a new type of Ohmic contact, i.e. AuGe on InP/GaAs-Al/Ni-P/GaAs, by chemical epitaxial growth. The growth of NiGeAs[P] grains is confined by these interfaces leading to an evident lateral grain expansion in GaAs or InP. The Au-containing grains selectively locate the InP/GaAs-Al/Ni-P/GaAs interface. Using a novel probe EDS, the composition of the NiGeAs grains in GaAs is determined to be 50% Ni, 33% As, and 17% Ge. In GaAs, the grains have 27% Ni, 29% GaIn, 4% As, and 14% Ge. The Au-containing grains at the InP/GaAs interface have a composition of 45% Au, 14% Ni, 16% Ga, and 28% As while the NiGeAs[P] grains annealed at a higher annealing temperature of 400°C for 3 hours, Au-containing grains expand laterally and are more by more Au diffusion from the contact. These TEM results can explain the fact that at higher annealing temperature, higher concurrence of the device is observed.

Electroplating experiments were conducted on a partially oxidized substrate in order to determine the interaction of the electroplating process with the substrate. In this study, we present a model for electroplating and the electrochemical reaction that takes place during the plating process. The model is based on electron holography and the exploitation of the chemically sensitive (002) reflection that is available in the low energy material. We apply an off-axis imaging condition where the specimen is tilted 4° along the (001) Kikuchi band. The (002) beam is strongly excited and centered on the optic axis. The first side band of the hologram is centered using an "empty" reference hologram obtained for a hole in the specimen. From the centered sideband we use the phase of the central (000) beam and the amplitude of the chemically sensitive (002) reflection to evaluate the local composition and the local specimen thickness in an iterative and self-consistent way. Delocalization effects that are caused by objective less aberrations and that lead to a shift of the spatial information of (000) and (002) reflections are taken into account. The applied procedure is demonstrated with an AlAs/GaAs(001) superlattice with a nominal period of 5 nm and a thickness of the AlAs layer of 2.5 nm. Our measurements reveal an edge-to-edge period of 4.86 nm. The (000) and (002) reflections reveal a total amount of AlAs of (2.5 ± 0.2) nm per AlAs layer. The concentration profiles obtained are discussed in relation to segregation. The measured segregation efficiency is R = 0.31 ± 0.02.

Lateral atomic ordering in p-type (carbon-doped) GaAs on (001) InP. Y.-Y. Park, E. Chevallier, O.J. Fiete, S.P. Watkins, K.L. Kavanagh, Dept. of Physics, Simon Fraser University, Burnaby, BC, CANADA. We have detected lateral ordering in p-type (carbon-doped) GaAs on (001) InP by conventional plan-view transmission electron microscopy (TEM) and CBED. The results of this comparative study showed that both TEM and CBED analysis obtained similar medium grain area values and grain orientations, but the TEM analysis measured higher medium grain area values. A detailed analysis of the CBED technique showed that the grain area distributions were weighted toward smaller grain areas due to scan step limitations, pixel resolution and the geometry of the tilt correction factor. When these corrections were applied, CBED analysis was found to overestimate the median grain area due to its inability to find small grain areas, e.g. grain areas < 0.4 μm^2 for a 0.1 μm scan step. The limitations and advantages of each method for grain size determination will be discussed in detail.
or superlattice spots in corresponding selected area diffraction (SAD) patterns. We observe two types of periodicities with twice or four times the usual lattice lattice parameter. The degree of ordering increases with growth temperature, as seen by increasing definition of the superlattice fringes in the images, and by a change from streaks to superlattice spots in the SAD patterns. While the formation mechanism is not yet understood, no differences were observed for samples in compression or tension. Since this particular type of ordering has not been previously reported in the literature, we will be investigating the samples further using a more powerful instrument. Standard high resolution microscopy, together with the above imaging techniques will give us more details about the structure. A proposed mechanism for the ordering similar to earlier work with MBE material [1] will be discussed. [1] I. Murgueitio, A. G. Norman and G. R. Booker, J. Appl. Phys. 67 (1990) 2110.

SESSION F6: SUPERCONDUCTING AND MAGNETIC MATERIAL
Chair: John E. Bonevich
Wednesday Afternoon, April 18, 2001
Salon 1.5 (Marriott)

1:30 P.M. *F6.1
SOLVING MATERIALS PROBLEMS WITH ELECTRON TEM AT HIGH SPATIAL RESOLUTION. Werner Gregorczyk, Kenneth M. Krishnan, Lawrence Berkeley National Lab, Nat. Sci. Dept., NCEM, Berkeley, CA; Dr. Sergio Sanchez, Carlos IV de Madrid, Depto Fisica, Madrid, SPAIN; Roger A. Ristau, Seagate Recording Media, Fremont, CA.

Energy-filtering transmission electron microscopy (EFTEM) has developed into a routine tool for chemical analysis on the nanometer scale. Combined with subsequent image processing techniques, EFTEM elemental distribution maps can be uniquely applied to solving materials problems at high spatial resolution. In this paper, two applications in magnetic (Cr distribution in recording media) and superconducting (growth mode of complex oxides) materials will be used to demonstrate recent developments, capabilities and limitations of the technique. The physical properties of thin films are strongly influenced by their growth mechanisms. In the case of complex ionic oxides, such as the superconducting cuprates, the growth mode (layer-by-layer or block-by-block) is not conclusively determined. In order to answer this fundamental question, an EFTEM study was carried out on specially prepared multilayer [YBa2Cu3O7x, /Pb2Cu2O37y, (where x is either an integer or non-integer) samples. Systematic imaging of non-integer YBCO/PBCO multilayers, utilizing the low energy loss ionization edges of Pb and Y, has conclusively shown evidence for the block-by-block growth mechanism. In CoCr based alloys used for longitudinal recording media, the recording performance is often impaired by the segregation of Co to the grain boundaries. It has been reported that the intergranular Co concentration can reach values high enough to render the alloy locally non-magnetic. This magnetic decoupling is responsible for better recording characteristics (higher signal to noise ratio). Post-acquisition image processing techniques (scatter diagram analysis) were applied to EFTEM elemental maps in order to quantitatively measure the amount of Cr segregation in CoCr based recording media. The segregation of Cr, measured globally in the sample, correlates well with the intergranular exchange coupling (M plots) and the signal to noise in the recording process.

2:00 P.M. *F6.2
ENERGY FILTERED IMAGING IN METALLIC MULTILAYER SYSTEMS. J. E. Bonevich, NIST, MSICE Lab, Gaithersburg, MD.

As the dimensions of devices approaches the nanometer scale, control of the composition and structure of thin films and their interfaces becomes crucial. In the case of magnetic spintronic devices, annealing can dramatically degrade GMR performance to almost zero accompanied by only minor structural variations. We have employed energy-filtered imaging (EFI) to characterize the extent of intermixing of magnetic and non-magnetic constituents on the atomic scale. Spin-valves with Co and Cu layers were annealed for 30 minutes at 380 C, causing the GMR to decrease from 30% to less than 5%. Intermixing of Co and Cu layers of only one to two monolayers was found sufficient to explain the diminished GMR values. Longer term annealing increased the degree of intermixing with an attendant structural modification. Intermixing of Co and Cu also dramatically affect the interface stress in multilayered systems. EFI and HREM characterization of highly textured [111] Ag/ Ni thin films has been employed in conjunction with the measurement of n-plane strain as a function of bilayer thickness. An interface stress of 2.02 GPa was measured for bilayer thickness greater than 5 nm. While for smaller bilayer interface stress no deflection of the interference of several monolayers. These results as well as EFI/HREM/TEM investigations of Al/Ti multilayered films will be presented.

2:15 P.M. *F6.3
QUANTITATIVE NANOMETER-RESOLUTION COMPOSITION MAPPING OF SEGREGATION IN Co-BASED THIN FILM MAGNETIC RECORDING MEDIA. J. Bentkover, Oak Ridge National Laboratory, Materials and Ceramics Div., Oak Ridge, TN; J. E. Wittig, Vanderbilt University, Nashville, TN.

The optimized performance of Co-Cr based thin film longitudinal magnetic recording media depends critically on the grain size distribution and on typically 3-nm-wide intergranular segregation of Cr (with concomitant Co depletion). These effects of the microstructure have been extensively investigated with quantitative elemental mapping by energy-filtered transmission electron microscopy (EFTEM). Procedures for data acquisition and processing have been refined in order to provide robust methods for measuring intergranular compositions for statistically significant numbers of grains. A recently devised 4-window method to extract reliable net Cr-L23 (575 eV) core-loss intensities in the presence of surface oxide (K edge at 522 eV) is an essential component of these procedures. Commonly in media with 12 to 15% Cr, maximum intergranular Cr levels are 34 ± 5%, and grain interiors may have <5% Cr. Unfortunately, Tb and Pt, which are important additional alloying elements, are not amenable to quantitative elemental mapping by EFTEM, but can be mapped by high-resolution energy-dispersive X-ray spectroscopy (EDS) performed in an analytical electron microscope (AEM) equipped with a field-emission gun (FEG). Simultaneous electron energy-loss spectrometry (EELS) and EDS spectrum imaging is therefore a useful complementary or alternative method for determining the local composition of the recording media, the distribution of other elements such as boron, of great interest. Reliable methods for quantitative boron mapping, either by EFTEM or EELS spectrum imaging, require the use of non-annular background subtraction procedures. The tails of the 3d transition metal M edge produce a background at the K edge [190 eV] that deviates from the usual inverse power law (AE~2). Log-polynomial background fitting procedures have been shown to yield reliable net B K edge signal intensities for quantitative composition measurement. Research at the Oak Ridge National Laboratory ShARE User Facility was supported by the Division of Materials Science and Engineering, US Department of Energy, under contract DE-AC05-000R22725 with UT-Battelle, LLC, and through the ShARE Program under contract DE-A10576OR04183 with Oak Ridge Associated Universities.

2:30 P.M. *F6.4

Nano-sized metal and oxide precipitates are of interest for e.g. dimension hardening, giant magnetic anisotropy and local research of interfacial structures. To this purpose we studied (magnetic) Co, Fe and CoPt precipitations in a Au matrix and MmO2 and ZnMnO precipitations in a Ag matrix using HREM, energy-filtered TEM and electron probe EDS. In a FEG-TEM. The development of the precipitates in the Au matrix as a function of growth conditions (temperature/time) was studied both in-situ and ex-situ. In the Ag matrix the Mn3O4 and Mn3O5 precipitates were reduced in-situ in the TEM to MnO and MnO/ZnO, respectively. The different crystal structures of the precipitates in the Au matrix, i.e. fcc Co, bcc CoFe and bcc CoPt result in markedly different precipitate shapes, orientation relations and interface orientations. These differences turned out to have large effects on the GMR effect, for example typical for superparamagnetic fluctuations. On the other hand the CoPt precipitates have a plane shape and a Bain orientation relation with the Au matrix. Under conditions of a thickness of about 5 nm and length of 40 nm they show a GMR effect approaching the spin-valve effect, as is seen in 3D plane-parallel TEM. For some advanced methods we have recently obtained the Mn3O4 and ZnMnO precipitates is that we could explain the observed reduction kinetics and Ostwald ripening of the Mn3O4 precipitates and show the important role of the strain development in the precipitates during reduction on the reduction kinetics. These strains could even prevent the reduction for a longer time.

2:45 P.M. *F6.5
VALENCE MAPPING OF MANGANESE OXIDE PARTICLES.
8:45 AM *FP7.1
SURFACE MICROSCOPY WITH SLOW REFLECTED AND EMITTED ELECTRONS. Ernst Bauer, Arizona State University, Tempe, AZ.

[ABSTRACT NOT AVAILABLE]

9:15 AM *FP7.2
STEP FLUCTUATIONS ON [011] SURFACES OF REFRACTORY METALS STUDIED BY LEEM. M. Ondrzejek, W. Swiech, R.S. Appleton, C.S. Durfee, G.W. Yang and C.P. Flynn, University of Illinois at Urbana-Champaign, Materials Research Laboratory, Urbana, IL.

Low-energy electron microscopy (LEEM) has been proven to be an excellent tool to study microtopography of surfaces on the nanoscale at variable temperatures. Its high temporal resolution has been recently employed for studies of step mobilities [1] on Mo and Nb surfaces. The [011] oriented samples have been grown heteroepitaxially on (1120) oriented sapphire substrates. Small micrometer-scale terraces with various azimuthal orientations were used. Experiments have been performed within the temperature range 1400K - 1700K. At lower temperatures Mo surfaces after an appropriate annealing procedure consist of almost parallel trains of monomolecular steps [2]. In contrast, steps on Nb (with submonolayer oxygen content) tend to bunch together and form nanofacets [3]. However, at temperatures above 1500K Nb facets separate into fairly straight single steps with the exception of the micromt exactly in the (1120) direction. In both cases, steps are not stationary. Large-scale oscillations of isolated steps have been recorded. The goal of the experiment was to investigate the time and wavelength dependence of the equilibrium step fluctuations as a function of element, temperature and substrate micromt direction. From amplitudes of the fluctuations, step stiffnesses can be determined. Quantitative details of step free energies and surface self-diffusion will be given in the talk.


9:30 AM *FP7.3
TOPOGRAPHIC CONTRAST FROM A PATTERED SEMICONDUCTOR SUBSTRATE IN LOW ENERGY ELECTRON MICROSCOPY. Hang-Chi Lee, R.J. Phaneuf, Laboratory for Physical Sciences, Department of Electrical and Department of MSE, University of Maryland, College Park, MD.

An ideal technique for inspection of ultra large scale integrated arrays of devices would combine fast acquisition, large field of view, high spatial resolution, and sensitivity to variations in composition, electrostatic potential and patterns associated in the sub-micrometer scale. Low energy electron microscopy (LEEM) provides video rate imaging of surfaces at resolution of several nm and is a particularly powerful potential inspection technique for such devices. At very low energies, LEEM is quite sensitive to surface corrugation. We report the first semi-quantitative measurement of the high topographical sensitivity of low energy electron microscopy operated at very low energy mode (VLEEM). As a simple prototype we patterned a Si(001) surface with a sub-micron dimension pit array. VLEEM Images of these pits consist of an array of bright spots whose diameters depend strongly on the energy of the incident electrons. Our electron-optical simulation shows that each pit locally perturbs the electric retarding field and causes strong electron-optical effect on the incident electrons, which produces strong "topographic contrast" in the image.

Work supported by the Laboratory for Physical Sciences and by NSF-MRSEC.

9:45 AM *FP7.4
THE SEM MIRROR METHOD: A NEW TOOl TO INVESTIGATE INSULATORS. J. Bégué, P. Hourgebe, CEA Le Ripault, FRANCE.

It is well known that it is very difficult to investigate the insulator materials with a Scanning Electron Microscope on account of the charge trapping that modify the electron trajectories and the contrast. To avoid these charge effects, the surface of the samples are often metallized. In the meantime, the charge trapping behavior is an intrinsic property of insulators and it very interesting to study it on a local scale. The SEM Mirror Method (SEMMM) was first developed
10 years ago to study the trapping and detrapping of charges in insulators. Electrons are directly injected with a high energy (for example 30 keV focused electron beam in spot mode). The quantity of injected charge is well controlled by measuring the beam current and the injection duration. Then, the image of the charged area is observed at low energy (typically 0.3 KeV) in scanning mode. On account of the trapped charge, the image in scanning mode is different from that in the secondary electron mode. To exam the charge' lifetime, the electron trajectories are strongly modified and can come back to the upper part of the chamber. Then, the image appears like a spherical mirror centered in the charged area where the detector and the gun exit image can be observed. The electron trapping and detrapping under the surface, the electron charge distribution with more complex analytical or numerical models. This technique has been used to study different insulators like ceramics (Quarts, pure and doped Sapphire, alumina, silicon) and polymers (polyethylene, polypropylene). Some correlation between charge trapping properties and microscopic behaviors (mechanical or electrical properties) have been established.

10:30 AM *FF7.5
ALCHEMI AND HOCUBOSCAL - FUNDING FOREIGN ATOM SITES IN MICROCRYSTALS: John Spencer, Arizona State University, Tempe, AZ.

The Atom Location by channeling enhanced microanalysis (Alchemi) method uses the electron-beam orientation dependence of characteristic X-ray emission from a thin crystal (due to diffraction) to determine the location of foreign atoms. More than 100 papers have now been described applications of this TEM-based method. This talk will review recent developments, and discuss practical application of the method to problems in geology, semiconductors, superalloys and oxides. Recent important advances, such as statistical alchemi and soft alchemi will be reviewed, together with two-dimensional alchemi (characteristic X-ray emission plotted as a function of collimated incident beam direction). The effects of localisation are summarised, and the challenge of ELS alchemi reviewed. Finally, a new method which allows two-dimensional X-ray alchemi patterns to be interpreted subject-specific holograms of the local environment will be described.

A summary of recent work can be found in Phil Mag A 74, p. 57 (1996).

11:00 AM FF7.6
HIGH ANGULAR RESOLUTION ELECTRON CHANNELLING X-RAY SPECTROSCOPY (HARECSX) AS A METHOD OF ESTABLISHING CATION DISPLACEMENT ENERGIES: Nestor J. Zohore, Argonne National Laboratory, Argonne, IL, Katherine L. Smith, Australian Nuclear Science and Technology Organisation, NSW AUSTRALIA.

Long-term radiation damage effects in waste forms due to alpha decay have been simulated either by doping with samples with short-lived isotopes or by heavy ion bombardment. Conversion of doses (in units of alpha/mg or ions/cm^2 s) into standard radiation damage units of displacement per atom (dpa) requires knowledge of the displacement energies (Ed) of all the ionic species of the target material. Various titannes have been proposed as host phases for immobilising actinide rich waste. To date, only the Ed values of cations in titannes have been examined. We have determined Ed values for all ionic species by an elaborate comparative estimation technique. These values should be used for other titannes. To date, we have collected data from fully amorphous perovskite and perovskite irradiated to 0.5 and 0.35 times the critical dose for full amorphisation (0.35 dc) of perovskite. The HARECSX signature of perovskite irradiated to 0.35 dc was significantly different to that of unirradiated perovskite. This data and HARECSX data for perovskite irradiated to 0.1 and 0.05 dc will be presented.

11:15 AM *FF7.7
AN IN-SITU MATERIALS DEVELOPMENT SYSTEM FOR SUPPORTED THIN FILM AND NANOPHASE MATERIALS: Mark W. Yelon, Materials Science Research Group, Oak Ridge National Laboratory, Oak Ridge, TN, and Dept of Mat Sci, Natl Univ of Singapore, SINGAPORE.

The electron microscope is well established in the analysis of thin films and nanomaterials due to the remarkable penetration of high energy electrons. From the earliest stages of its development, in-situ experiments have been performed in the transmission electron microscope and remarkable observations have been made with a variety of different stages and environments. In-situ experiments have complimented ex-situ investigations in solving a number of significant materials issues. Owing to significant developments in vacuum technology since the 1950's it is now possible to construct electron microscopes capable of operating in UHV design rules, with stable base pressures below 2.10^-9 Torr. Surface science studies, and in-situ thin film growth studies (molecular beam epitaxy, sputtering) may thus be performed almost routinely with appropriate sample geometries. In this talk, I will describe a Development blank, located on the campus of the National University of Singapore. The system comprises a JEOI 2000IV ultrahigh vacuum transmission electron microscope with in-situ BSE, sputtering and gas dosing capability. Studies of supported metal nanocrystals will be described, together with a study of the growth of nitride thin films on the clean Si surface.

SESSION FFS: CERAMIC MATERIAL
Chair: James Bentley
Thursday Afternoon, April 19, 2001
Session 15 (Marriott)

1:30 PM FFS.1
INCORPORATION OF LARGE CERIUM IONS INTO THE ALPHA-SIALON STRUCTURE: Fang-Fang Xi, Yoshihito Hendo, Chang-Ming Wang, Masanori Miomoto, Nihon-Tsubaki, JAPAN.

Al2O3-Cu is a structural derivative based on the aluminosilicate structure by partial replacement of Si by Al and N by O. The structure is considered to be stabilized by the incorporation into the large interstices (r=0.146nm) of a metal like Li, Mg, Ca and small Rare earth metal ions have been considered not to be able to enter the interstices of the alpha-sialon structure until several recent successes in accommodating large cerium ions (r=0.187nm). This gives rise to the question of the location and distribution of these large cerium ions within the aluminosilicate structure. The Ce-doped alpha-sialon material was prepared in our present work and has been examined by field-emission transmission electron microscope (STEM) equipped with energy dispersive spectroscopy (EDS). TEM observations revealed that almost all the aluminosilicate grains contain high densities of domain boundaries, the type of which could never be discovered in silicon nitride or silicon material doped with small metal ions. The domains are embedded by some specific faces in this strongly-bonded covalent compound, i.e. the (0001), 711 and the surface with the smooth crystal on the 110 direction. The conventional diffraction contrast analysis suggests that these domains be formed by a single translation of 1/3x16x0 type. The chemical composition has been examined by EDS microanalyses. It is then discovered that majority of the incorporated cerium ions segregate toward the domain boundaries. Structural modelling finally gives a clear interpretation of this structural configuration, i.e. the translation has brought about the enrichment of interstitial Cs' ions into an atomic layer along c-axis in the domain boundary region. This, together with the lattice expansion normal to c-axis, has produced enhanced interstices which become able to accommodate large metal ions like Ce.

1:45 PM FFS.2
MORPHOLOGY, MICROSTRUCTURE AND DEFECTS IN FUSED SILICA INDUCED BY HIGH POWER 3w (355 NM) LASER PULSES: Joe Wang*, D. Haupt*, J. H. Kinney*, M. Stevens-Kalchoff* and A. Steensma*, J. Ferriera*, F. Lindsey* and I. Hutchens, Lawrence Livermore National Laboratory, University of California, Livermore, CA. 1Department of Applied Physics, University of Technology, Sydney, NSW, AUSTRALIA. 2Department of Physics, University of Leuven, Leuven, BELGIUM.

The morphology and microstructure of damage sites in high quality fused silica induced by high power UV (355nm) laser pulses have been investigated using a suite of electron microscopies and microscopic tools. These include SEM, HREM, microprobe analysis, XPS, SIMS and x-ray microtomography utilizing intense synchrotron radiation. Systematic SEM examinations show that the damage sites consist primarily of a molten core region (thermal explosion) surrounded by a concentric region of fractured material. The latter arises from propagation of lateral cracks induced by the size of the overall crater, dependent on laser fluence, number of pulses, irradiation history and environment. In particular, differences in morphology of the damage sites are identified: air vs. vacuum, exit (more severe) vs. entrance surface, and regular polish (more severe) vs. super polish surfaces. A completion layer, ~10 microns thick and ~20% higher in density has been identified with x-ray tomography. High resolution microprobe analysis shows that there is no variation in the Si/O
With the high energy-resolution of a FEG analytical electron microscope, spatial difference technique can be applied to the investigation in ceramics, more accurately, more reliably and no longer subjective. An analog to the mathematically more complicated multi-variant statistical analysis method provides the basis for the reliability. This approach leads to further and valuable quantitative information about the grain boundary and interface. The successfulness of this analysis depends on comprehensive and systematic investigation of the ELNES of the relevant system as well as thoroughly evaluation of the detector property. These guide lines enable an accurate separation of interfacial electronic features 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 approach can reach the best performance and evaluation allowed by the probe size. An effective probe size can also be deduced. Examples are given from non-oxide structural ceramic systems like silicon nitride and carbides where a nanometer-thick amorphous film is often seen in grain boundary. However, this method could be also applied in other interfacial phases. For special and other non-wetting boundary, such spectrum separation approach can define a region for grain boundary by its ELNES properties and can provide a new angle to evaluate these boundaries.

3:30 PM **FF8.6 QUANTITATIVE OXYGEN VACANCY ORDERING AND SEGREGATION IN PEROVSKITES BY HIGH TEMPERATURE ATOMIC RESOLUTION TRANSMISSION ELECTRON MICROSCOPY** N.D. Browning and R.F. Klie, University of Illinois at Chicago, Department of Physics, Chicago, IL.

Many of the transport properties of perovskite oxides are controlled by the presence of oxygen vacancies and in particular, whether these vacancies form ordered phases or segregate to defect sites. The experimental conditions for obtaining transmission electron microscopy (STEM) images and energy loss spectroscopy (EELS) is demonstrated in an ion conductor, the key to transport is the formation of a highly oxygen deficient material. In-situ experiments show that above a specific temperature ordered phases begin to form. The energetic of oxygen vacancy formation are different for different sites in this ordered structure, which means that once it is nucleated it continues to expand. Furthermore, the ordered phase itself does not appear to be the major factor limiting oxygen mobility, it is domain size that is important. The second system studied is grain boundary in SrTiO3. Here results indicate that there is a segregation of oxygen vacancies to the boundary plane that results in the formation of a highly oxygen doped region. Such results are consistent with in-situ simulations and give the features of SrTiO3 of great to be proven in perovskites, explains the widely observed transport properties of many polycrystalline perovskites.

4:00 PM **FF8.7 Abstract Withdrawn**

4:15 PM **FF8.8 MICROANALYSIS OF POLYPYROID FUNCTIONAL GRADIENTS FOR JOINING DISILLAR CERAMICS: SiN4-Al2O3 SYSTEM** Caroline S. Lee, University of California at Berkeley, Dept. of Materials Science, Lawrence Berkeley Laboratory, Berkeley, CA. Xing-Feng Zhang, Materials Sciences Division, Lawrence Berkeley Laboratory, Berkeley, CA. and Andrew D. Pearson, Department of Materials Science, Lawrence Berkeley Laboratory, Berkeley, CA.

A unique approach to crack-free joining of heterogeneous ceramics is demonstrated by the use of polypypoids as Functionally Graded Material (FGM) in the system, SiN4-Al2O3. Polypypoids in the Al2O3-SiN4 system offer a path to compatibility for heterogeneous ceramics for the following reasons. The CTE of all such Polypypoids is intermediate between that of SiN4 and Al2O3, and is approximately chemically compatible with both SiN4 and Al2O3. These compounds also have glassy interfaces, which can give good thermal stability. Amorphous Polypypoids are plane faulted structures based on the hexagonal 2H structure, and its fault periodicity and spacing is fixed by the cation/anion ratio. A set of these varying faults determines the effective strain. An FGM joint of SiN4 and Al2O3 using 12H Polypypoid interlayer has been fabricated using 200nm amorphous layers. This FGM is fabricated by powder blending, powder stacking and sintering
using Hot Press. To produce this crack-free joint, 20 layers with thickness of 300 µm each, were stacked to minimize thermal residual stress. High Resolution Electron Microscopy is used to identify the polytypoids at interfaces of different areas of the joint by looking at their diffraction patterns. It has been found that the 15R polytypoid was formed at the interface of Al₂O₃-rich area and 12H polytypoid was formed at the interface of Si₃N₄-rich area. To detect glassy free interfaces, High Resolution Electron Microscopy is also used to look at various grain boundaries. Therefore, electron microscopy plays a crucial role in my research because of their specificity and high spatial resolution.

4:30 P.M. F28.9
YITTRIUM SEGREGATION IN HIGH PURITY SUPERPLASTIC Y-TZP: SIGNIFICANCE IN TENSILE CREEP. Sini S. Soni, Terence G. Longdon, University of Southern California, Department of Materials Science and Aerospace and Mechanical Engineering, Los Angeles, CA; Neal D. Evans, James Bentley, Oak Ridge National Laboratory, Metals and Ceramics Division, Oak Ridge, TN.

Constant stress tensile creep tests were performed on samples of high purity superplastic yttria-stabilized zirconia (Y-TZP). The results revealed an immediate steady-state condition with a gradual decrease in the creep rate evident after large strains. This decrease became more significant with a decrease of the applied stress. At the lowest testing stress, the appearance of the creep curve resembled a primary creep region. These results were related to a diffusional creep mechanism controlled by interface reaction. Analysis of grain boundary chemistry and morphology were necessary to relate the deformation behavior to interface phenomena in this material. Scanning Transmission Electron Microscopy (STEM) was utilized to inspect and characterize grain boundaries at high magnifications. The probe current was set at 1 nA and the probe size was ~2 nm FWHM. Energy-Dispersive X-ray Spectroscopy used with STEM in these conditions allowed the detection of yttrium enrichment within ~2 nm of the grain boundary. It is possible that the yttrium present in grain boundaries exerts a drag on the grain boundary dislocations and limits their mobility. In this case, the creep rate is proportional to the dislocation mobility. Therefore, a continuous decrease in the mobility of grain boundary dislocations due to yttrium segregation may be the origin of the continuous decrease in creep rate.