SYMPOSIUM FF

Materials Problem Solving with the Electron Microscope

April 17 – 19, 2001

Chairs

Ray D. Twesten
Seitz Materials Research Lab
Univ of Illinois-Urbana
Urbana, IL 61801-2985
217-244-6177

James Bentley
Metals & Ceramics Div
Oak Ridge National Laboratory
MS-6376 Bldg 5500
Oak Ridge, TN 37831-6376
865-574-5067

Ulrich Dahmen
Lawrence Berkeley Natl Lab
NCEM - MS 72-150
Berkeley, CA 94720
510-486-4627

J. Murray Gibson
Matls Sci Div
Argonne Natl Lab
Argonn, IL 60439-4838
630-252-4925

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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 Spence, 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 magnetic imaging using both probes. Examples 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-Xray 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 1990 a hexapol-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 200 kV TEM equipped with a 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 1.0 ngstrom can be achieved for an accelerating voltage of U = 200 kV. In the case of a 300 kV TEM and an energy width of dE $<$ 0.2 eV a point resolution close to 0.5 ≈ can be approached. The main advantage of spherical aberration correction is that structure-imaging artefacts due to contrast delocalization can be avoided to a great extent [5]. These artefacts have turned out to be a major obstacle for the application of FEG instruments to defect and interface studies. Contrast delocalization arises from the width of the aberration discs belonging to the individual diffracted electron waves whose diameter increases with Cs. The first applications of this corrected TEM have been carried out in the group of K. Urban at the Research Center Juelich.
[1] Rose H., Optik 85 (1990) 19.
[2] Haider M., Uhlemann S., Schwan E., Rose H., Kabius B. and Urban K., Nature 392 (1998) 768.
[3] Uhlemann S. and Haider M., Ultramicroscopy 72 (1998) 109.
[4] Haider M., Rose H., Uhlemann S., Schwan E. Kabius B. and Urban K., Ultramicroscopy 75 (1998) 53.
[5]Haider M., Rose H., Uhlemann S., Kabius B. and Urban K., J. Electron Microsc. 47 (1998) 395.

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

Scanning transmission electron microscopes (STEMs) have several major advantages over conventional (broad beam) electron microscopes (CTEMs): 1) they work best in the incoherent high-angle dark field (HADF) imaging mode, which gives 40% 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 other properties of the sample, 3) they are less sensitive to the effect of chromatic aberration, and 4) their optics is simpler because they only have to focus the electrons into one narrow beam rather than form an image of many points simultaneously. The major limit on the performance of STEMs is typically due to the spherical aberration of their objective lens. A spherical aberration (C_s) corrector allows C_s to be set to a very small value (typically a few tens of microns) that best counteracts the effect of higher order aberrations (such as C_5). It typically allows the resolution to be nearly doubled and the beam current in a given probe-size 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_s-corrected STEMs to image and analyze real-world samples, and point out the directions aberration-corrected STEMs are likely to take in the future. Among other conclusions, we will show that a C_s 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 Rühle 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 relaxations occur quite close to the interfaces it is important to carry out the investigations with high spatial resolution: the atomistic structure of specific (tilt) interfaces can be determined by high-resolution transmission electron microscopy studies (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-eV-sub-Angstroem-Microscope) built by LEO 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 $\leq$ 0.2 eV. A MANDOLINE energy filter will be installed allowing for a much higher transmissivity as compared to conventional Omega filters or Gatan imaging filters.

11:00 AM *FF1.5
APPLICATION OF SPHERICAL-ABERRATION CORRECTED TRANSMISSION ELECTRON MICROSCOPY TO MATERIALS SCIENCE. K. Urban, J.H. Chen, C.L. Jia, M. Lentzen, M. Luysberg, A. Thust, Institute for Microstructure Research, Research Center Juelich, Juelich, GERMANY.

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 supertwin lens exhibits a point resolution close to the information limit of about 0.135∼nm using the standard double-tilt stage with $\pm 40°$ 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 delocalisation. 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_s the contrast for high resolution can be selected with respect to phase-contrast ($C_s>0$) and amplitude-contrast ($C_s \approx 0$)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 perovscite materials, Si/silicide and compound semiconductor heterostructures will be presented.
[1] M. Haider, H. Rose, St. Uhlemann, E. Schwan, B. Kabius and K. Urban, Nature **392**, 768 (1998).

11:30 AM FF1.6
ABERRATION-CORRECTED MICROSCOPE DESIGN FOR LARGE-GAP IN-SITU ELECTRON MICROSCOPY. Kai Xiu, 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 experiment [1]. Using current design for spherical aberration (Cs) correction [2], we will discuss the optimum performance available as a function of gap size. Calculations include realistic lens configurations and the effect of instabilities and stray fields. Ultimate performance could 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 haxapole-quadrupole-octopole corrector. Analysis includes consideration of off-axis aberrations, fifth-order axial aberrations and use for STEM and for TEM.
References:
[1] J. Murray Gibson, National Transmission Electron Achromatic Microscope, a preproposal for a national microscopy project (2000).
[2] H. Rose, Nucl. Instrum. Methods, 187, 187 (1981).

SESSION FF2: AMORPHOUS AND NANOPHASE MATERIALS

Chair: Paul M. Voyles
Tuesday Afternoon, April 17, 2001
Salon 15 (Marriott)

1:30 PM *FF2.1

VOLUMETRIC CHARACTERISTICS OF NANOSTRUCTURED POLYMER SYSTEMS BY TRANSMISSION ELECTRON MICROTOMOGRAPHY. Richard Spontak, North Carolina State Univ, Depts of Chemical Engineering and MS&E, Raleigh, NC; Hiroshi Jinnai, Kyoto Inst of Technology, Dept of Polymer Science & Engineering, Kyoto, JAPAN; David Agard, Univ of California, Depts 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 regarding such systems, their volumetric characteristics remain elusive. In this work, we demonstrate how transmission electron microtomography (TEMT) 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 morphologies 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 spheres as they strive to reach equilibrium as cylinders upon crossing the sphere-to-cylinder order-order transition. The in-situ morphology of biphasic polymer latex particles generated in supercritical CO2 will also be addressed here through the use of TEMT.

2:00 PM *FF2.2

FLUCTUATION MICROSCOPY AS A PROBE OF MEDIUM RANGE ORDER. M.M.J. Treacy, NEC Research Institute, Inc., NJ; P.M. Voyles, Lucent, Murray Hill, NJ; J.M. Gibson, Argonne, IL; J.E. Gerbi and J.R. Abelson, U. Illinois, IL.

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 disordered materials, as a function of hollow cone angle. This method is also called variable coherence microscopy. The speckliness of an image 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 simpler diffraction techniques fail. I will also present experimental observations of medium range order in amorphous silicon and germanium films.

2:30 PM *FF2.3

CHARACTERISATION OF AMORPHOUS MATERIALS BY ELECTRON DIFFRACTION. David J.H. Cockayne, William McBride, Univ of Oxford, Dept of Matls, Oxford, UNITED KINGDOM.

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 using energy selected electron diffraction is now established as the most reliable tool for characterizing these materials. It can be used to differentiate between possible candidate structures; it can give nearest neighbour distances to an accuracy of 0.02 nm; and it can be applied to the refinement of structural models derived from ab-initio or other modelling approaches. The technique can be used not only for single element materials, but also for alloys, provided that limitations inherent in the interpretation of the data are appreciated. Recent advances, including the two dimensional collection of the diffraction pattern using image filtering systems, give increased sensitivity, while deconvolution of the incident probe function from the diffraction data allows the use of incident beams approaching the nanometer dimension. These advances open up the possibility of investigating small amorphous volumes as found, for example, in intergranular films, in volumes amorphised during device fabrication and in layered structures.

3:30 PM FF2.4

DETERMINING ATOMIC POSITIONS IN ZrO_2 and TiO_2 NANOCRYSTALS BY FOCAL-SERIES EXIT WAVE RECONSTRUCTIONS. Jane F. Bertone, Timothy J. Trentler, Vicki L. Colvin, Department of Chemistry, Rice University, Houston, TX; Christian Kisielowski, National Center for Electron Microscopy, Lawrence Berkeley National Laboratory, Berkeley, CA.

In general, the precise atomic structure of a nanoparticle can be difficult to measure. However, since such samples are quite thin, superior quality high-resolution electron microscopy (HREM) images can be obtained from them. With the advent of holographic reconstruction techniques, analysis of HREM data has become a quantitative measurement. This allows for the investigation of nanocrystal structure and strain. In this investigation, chemically synthesized oxide nanocrystals, of diameters <10 nm, were studied using high-resolution electron microscopy (HREM) and object exit wave reconstruction. We have retrieved exit wave functions of titania and zirconia nanocrystals using Philips/Brite-Euram software for focal-series reconstruction. The atomic positions across particles were investigated and compared to simulated exit wave functions. In some cases reconstruction quantified the distance between an oxygen atom and its bonded metal neighbor. Additionally, particle shape was studied.

3:45 PM FF2.5

SURFACE STRUCTURE CERIANITE NANOCRYSTALS: TEM INVESTIGATION. Huifang Xu, TEM Laboratory, Dept of Earth & Planetary Sci, Univ of New Mexico, Albuquerque, NM.

Surfaces of crystalline materials may reorganize to energetically stable structures that are different from their bulk structures (e.g., (111) and (5 5 12) of silicon). TEM can be used for characterization of such kinds of surface structures, such as (5 5 12) surface of silicon. Ce(IV) oxide (cerianite) nanocrystals that were considered as chemical analog of Pu(IV) oxide colloids in polluted groundwater have been studied using HRTEM EELS. Dominant surfaces of the nanocrystals are {100} and {110}. Curved surface are caused by combination of two groups of surfaces (e.g., (100) and (111)) that form surface steps. HRTEM images show the surface layer with thickness of one unit-cell forms a superstructure with respect to Ce(IV)-oxide bulk structure. The periodicities of the superstructure along <100> and <111> directions are about doubled with respect to the bulk substructure. It is proposed that the superstructure is resulting from oxygen deficiency in the surface layer. Oxidation states of some Ce atoms on the surface may be in the form of Ce(III). EEL spectra of oxygen K-edge and Ce M-edges show the difference between bulk crystals and the surface layer. It is proposed that electronic structure for oxygen atoms on the surface and in bulk crystal are different. A structure model for the surface layer is also proposed.

4:00 PM FF2.6

CHARACTERIZATION OF THE LOCAL COMPOSITION AND CHEMISTRY OF TITANIUM CARBIDE COATINGS. Ernesto Coronel, Martin Saunders, Urban Wiklund, Eva M. Olsson, Uppsala University, The Ångström Laboratory, Uppsala, SWEDEN.

A multilayer physical vapour deposition (PVD) process for the deposition of titanium carbide coatings has been developed by researchers in the Department of Materials Science, Uppsala University, Sweden [U. Wiklund, M. Nordin, O. Wänstrand, M. Larsson, Surface and Coatings Technology **124** (2000)]. This process involves the successive deposition of electron beam evaporated titanium and dc magnetron sputtered carbon. Coatings, approximately two microns thick, with various Ti:C ratios have been deposited onto high speed steel. A thin titanium layer has been deposited initially to improve the adhesion of the surface coating to the steel substrate. The mechanical and tribological properties of the coating can be tailored to specific requirements by adjusting the Ti:C ratio. Initial characterization of the coatings via a combination of x-ray diffraction and transmission electron microscopy (TEM) has shown that the microstructure changes significantly with the Ti:C ratio. For low carbon content ($\sim$ 40at%), the coating consists of textured, columnar TiC_x grains a few hundred nm in diameter extending perpendicularly from the steel substrate. For high carbon content ($\sim$ 60at%), the coating consists of randomly ordered TiC_x grains a few nm across embedded in an amorphous matrix. Further studies are now underway to investigate the fine scale microstructure of the coatings. These investigations are being carried out using a Fei/Philips Tecnai F30ST FEG-TEM equipped with a Gatan Imaging Filter, EDAX EDS system, and BF/DF and HAADF STEM detectors. Energy-filtered imaging, and a combination of electron energy-loss and and energy-dispersive x-ray spectrum-imaging, have been used to characterize compositional and chemical variations at the nanometre

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-loss spectra arising from the TiC_x grains and the amorphous matrix in the high-carbon material.

4:15 PM FF2.7
DIFFRACTION FROM SMALL VOLUMES: SILICON NANOPARTICLES. R.D. Twesten, Seitz Materials Research Lab, Center for Microanalysis of Materials, Urbana, IL; Lubos Mitas, North Carolina State Univ., Dept of Physics, Raleigh, NC; G.A. Belomoin and M.H. Nayfeh, Univ of Illinois, Dept of Physics, Urbana, IL.

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-inito 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-inito calculations, we are investigating this system using electron diffraction. Comparing simulated diffracted intensities of relaxed and unrelaxed '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 subnanometer 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 strong scattering of the carbon support film. We are currently conducting both 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 DEFG02-96ER45439.

4:30 PM FF2.8
THE EFFECT OF VANADIUM ADDITION ON MICRO-STRUCTURES OF ULTRAFINE GRAINED LOW CARBON STEEL MANUFACTURED BY ECA PRESSING. Sangmin Kim, Jongryoul Kim, Donghyuk Shin, Hanyang Univ, Dept of Metallurgy and Materials Engineering, Ansan, Kyunggi-Do, KOREA (SOUTH).

Ultrafine grained (UFG) low carbon steels manufactured by ECAP demonstrated excellent mechanical properties, especially high yield strength. For practical applications, the UFG steels possess low yield ratio due to that severe plastic deformation accumulates extensive internal energy inside materials, which requires heat treatment for the relief of residual stress. However, it is difficult to control the grain size during heat treatment due to that the structural inhomogeneity 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 TEM have been used to investigate the microstructural evolution of the steels with different vanadium contents during ECAP. According to results, the effects of vanadium additions on the microstructure of the steels produced by ECAP are as followed; 1) Iron carbides, which existed in pearlite, were observed to be evenly distributed the whole ferrite boundaries of a sample after ECAP, whereas they were found in the vicinity of pearlite without vanadium. 2) Coherent vanadium precipitates were nucleated heterogeneously at 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 precipitates affect recrystallization behaviors. 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 $\sim 3\ \mu m$ and 87 % 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 HREM and TEM.

SESSION FF3: POSTER SESSION
DOE SHARED ELECTRON BEAM CHARACTERIZATION FACILITIES

Chair: Ray D. Twesten
Tuesday Evening, April 17, 2001
8:00 PM
Salon 1-7 (Marriott)

FF3.1
MATERIALS CHARACTERIZATION VIA THE SHARED RESEARCH EQUIPMENT USER FACILITY AND PROGRAM. Neal D. Evans, Oak Ridge Institute for Science and Education, Oak Ridge, TN; Ian M. Anderson, James Bentley, Edward A. Kenik, Michael K. Miller, and George M. Pharr, Oak Ridge National Laboratory, Oak Ridge, TN.

State-of-the-art microcharacterization is often critical in solving challenging materials problems, but researchers may not have access within their own institution to the required specialized capabilities. The DOE User Facilities help to address this need. The Shared Research Equipment (SHaRE) User Facility (http://www.ornl.gov/share) at Oak Ridge National Laboratory includes a variety of advanced electron microscopes with capabilities such as energy-filtered transmission electron microscopy (EFTEM), energy-dispersive X-ray spectrometry (EDXS), electron energy-loss spectrometry (EELS), spectrum imaging, low-voltage scanning electron microscopy (SEM), orientation imaging microscopy (OIM), and texture mapping. The large microanalysis data sets are commonly analyzed by advanced statistical methods. Special holders are available for in situ deformation and annealing studies. Extensive specimen preparation methods (e.g., electropolishing, ion milling, focused ion beam milling) are available.
Other complementary characterization capabilities available within the SHaRE Facility include atom probe field-ion microscopy (APFIM) and atom probe tomography (APT) for atomic-resolution elemental analysis in three dimensions, and mechanical properties microanalysis (nanoindenters). The expertise of the SHaRE Facility staff is a significant resource available to collaborative projects involving external researchers from academia, industry, other federal laboratories, and foreign institutions. Access is administered through the SHaRE User Program on the basis of a short research proposal. Except for proprietary research, there is no cost to the user. Grants are available to help defray costs of travel and accommodations for researchers from accredited U.S. universities. Examples of how the advanced analytical capabilities of the SHaRE facility have been used to address specific materials problems, and how access to the facility is obtained, will be presented.
Research at the Oak Ridge National Laboratory SHaRE User Facility is sponsored by the Division of Materials Sciences and Engineering, U.S. Department of Energy, under contract DE-AC05-00OR22725 with UT-Battelle, LLC, and through the SHaRE Program under contract DE-AC05-76OR00033 with Oak Ridge Associated Universities.

FF3.2
THE NATIONAL CENTER FOR ELECTRON MICROSCOPY: A USER FACILITY FOR MATERIALS CHARACTERIZATION AT ULTRA-HIGH RESOLUTION. C. Kisielowski, E. Stach, H. Poppa and U. Dahmen, National Center for Electron Microscopy, Lawrence Berkeley National Laboratory, Berkeley, CA.

The NCEM is a Department of Energy user facility for electron beam microcharacterization at Berkeley Laboratory. The facility hosts about 200 scientists annually. Use of its equipment is free of charge. The Center's array of unique instrumentation includes the One-Angstrom Microscope, the Atomic Resolution Microscope and a Spin Polarized Low Energy Electron Microscope (SPLEEM). These instruments are supported by a number of state-of-the-art electron microscopes and complemented by a sample preparation facility and a computational facility for image processing and quantitative analysis. In addition, experiments can be performed in-situ with uniquely designed sample holders. The present contribution highlights recent applications to advanced materials from users of the facility. They include imaging of the light elements carbon, nitrogen and oxygen with phase contrast microscopy at sub-Angstrom resolution, an investigation of physical properties of nanocrystals, and the segregation of impurities to specific sites at a grain boundary. Applications of piezoelectrically controlled manipulation and nanoindentation holders to the study of nanotubes and deformation in thin films will be demonstrated. Moreover, examples from recent research with the SPLEEM will illustrate the capability for real-time imaging of surface magnetic behavior during thin film growth. The selection of research examples will highlight the key role of electron optical techniques in the characterization of nanoscale materials.
NCEM is supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No.DE-ACO3-76SFOOO98.

FF3.3
THE CENTER FOR MICROANALYSIS OF MATERIALS: A NATIONAL USER FACILITY FOR *IN-SITU* MATERIALS SCIENCE. R.D. Twesten, I. Petrov, Univ of Illinois, Fredrick Seitz Materials Research Lab and the Materials Science Dept, Urbana, IL.

The Center for Microanalysis of Materials (CMM) is a major repository of instrumentation and expertise focused on the

nanocharacterization of materials using a full array of modern analytical techniques including electron microscopy, scanning probe microscopy, surface microanalysis, x-ray scattering, and ion-beam spectroscopies. The CMM places strong emphasis on *in-situ* materials science and has developed several unique instruments permitting dynamic studies in surface, interface, and thin film science under ultra-high vacuum as well 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 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 straining, an UHV high-temperature (>1800K) LEEM with MBE facilities, a variable-temperature (20-1600K) UHV STM with *in-situ* deposition, ion-irradiation, and gas-dosing, an *in-situ* film growth/imaging XPS, and cryogenic temperature/high magnetic field XRD. Here, we will highlight materials problem solving enabled by the CMM. Contributions will include ground-breaking research on surface crystallography, nanotopography evolution, and surface diffusion kinetics in heteroepitaxial refractory metals and refractory transition-metal nitrides, structure and reactivity relationships of catalysts for direct methanation fuel cells, and the interaction of hydrogen the dislocations.
The Center for Microanalysis of Materials is supported by the US DOE under grant DEFG02-96ER45439.

FF3.4
EXPANDING THE FRONTIERS OF MICROANALYSIS: RESEARCH AND DEVELOPMENT AT THE ELECTRON MICROSCOPY CENTER AT ARGONNE NATIONAL LABORATORY. Dean J. Miller, The Electron Microscopy Center, Materials Science Division, Argonne National Laboratory, Argonne, IL.

The Electron Microscopy 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 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 evolution of state-of-the-art 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 Yeadon
Tuesday Evening, April 17, 2001
8:00 PM
Salon 1-7 (Marriott)

FF4.1
EFFECTS OF ELASTIC WAVES ON ANNULAR DARK-FIELD STEM IMAGE. Kazutaka Mitsuishi, Masaki Takeguchi, Hidehiro Yasuda and Kazuo 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 Z contrast. Therefore, images obtained from ADF-STEM are expected to be intuitively interpreted with no contrast reversals along with the defocus and/or specimen thickness changes, in contrast with phase contrast images from HRTEM. 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 diffracted beams and/or channeling of probe electron may play an important role in the image. Therefore, the appropriate selections of parameters, such as defocus and detector angles are essential in ADF-STEM observations. It means that the image simulation of ADF-STEM image is still needed in order to achieve the appropriate incoherent imaging condition. Recently, many trial to measure the impurity density and/or positions from slight intensity difference of ADF-STEM is being performed, so that a demand for the accurate and fast simulation method is increasing, and those theoretical analyses are studied by several authors. Recently, authors presented new scheme of calculation which can evaluate elastically diffracted beam intensities together with TDS intensities. Using this method, the features and effect of elastically diffracted 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. Kazutoshi Kaji, Takashi Aoyama, Hitachi Research Labratory, Hitachi Ltd., Ibaraki, JAPAN; Shunroku Taya, Hiroyuki Tanaka, Shigeto Isakozawa, Instruments Group, Hitachi Ltd., Ibaraki, JAPAN.

A new type of elemental mapping system which consists of a two-window energy filter and a scanning transmission microscope has been developed. The energy filter has two kinds of electron beam detectors. One is a dual detector unit for observing elemental 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 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 Phillipp, Max-Planck-Institut fuer Metallforschung, Stuttgart, GERMANY; Joerg Porsche, Ferdinand Scholz, 4. Physikalisches Institut, Universitaet 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 specimens were grown by low pressure metal organic vapor phase epitaxy (MOVPE) on (001) GaAs substrates with different orientation angles toward the next $(111)_B$ -plane using the Stranski-Krastanow growth mode. Choosing appropriate growth parameters, the deposition of 3.4 monolayers InP on GaInP leads to the nucleation of coherently strained, small quantum islands due to the misfit of 3.7 % . Investigating the vertical stacking behavior of threefold stacks of InP quantum dots, has led us to introduce a correlation function which describes the correlation of island position alignment between one buried InP layer and the next. The coarse of maximas of the correlation angle distribution as 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 JEOL 4000 - FX 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 modus. We found an increasing correlation-angle for quantum dot multilayers 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.

FF4.4
COMPOSITIONAL ANALYSIS OF GRADED $Al_xGa_{(1-x)}As$ LAYERS BY X-RAY ENERGY DISPERSIVE SPECTROMETRY. Krishnamurthy Mahalingam, Robert Wheeler, Waltrud T. Taferner, Kurt. G. Eyink, Steve T. Fenstermaker.

Compositionally graded $Al_xGa_{(1-x)}As$ layers are important materials for graded-index wave guide 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 (XEDS) technique to characterize a variety of $Al_xGa_{(1-x)}As$ layers with linear, parabolic and sinusoidal grading in the Al content. The individual layers were grown by molecular beam epitaxy, with film thickness and composition monitored in-situ by spectroscopic 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 Cliff-Lorimer (CL) equations, assuming the thin-foil criterion. The so called k-factors in the CL equations (k_{Al-As} , k_{Ga-As} and k_{Al-Ga}), required for calculating the composition profiles, were determined from pre calibrated $Al_xGa_{(1-x)}As$ layers. Further details on the comparison between XEDS results with those obtained from SIMS, AES and the SE will be presented. The application of XEDS to identify film growth related problems, such as flux transients, will also be discussed.

FF4.5

TEM STUDIES ON $CoSi_2$ AND $NiSi_2$ FORMATION. M. Falke, S. Teichert, H. Giesler, B. Gebhardt, G. Beddies, H.-J. Hinneberg, Inst of Physics, Tech Univ Chemnitz, Chemnitz, GERMANY.

$CoSi_2$ and $NiSi_2$ are stable silicides with CaF_2 structure and lattice constants close to that of Si. Difficulties in providing the C54 phase of $TiSi_2$ 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 a better understanding of silicide growth in these systems on a nm-scale. We will present some examples of detailed TEM studies in this field partly related to RBS and electrical measurements. The $CoSi_2$ growth by solid phase reaction of Co films with $Si_{1-x}C_x(001)$ substrates (x = 0, 0.001 and 0.005) and of Co/Ti- and Co/Hf-bilayers with Si(001) substrates in N_2 atmosphere was investigated. TEM on the $Co/Si_{1-x}C_x$ 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 noteworthy. RBS and electrical measurements showed a shift of the CoSi to $CoSi_2$ transformation temperature to higher values with rising x. TEM investigations on the $CoSi_2$ growth on pure Si using Ti or Hf as diffusion barrier forming metals showed, that the formation of epitaxial $CoSi_2$ films proceeds through an intermediate textured CoSi-phase. The epitaxial $CoSi_2$ was found to nucleate at the CoSi/Si-interface with a more pronounced delay compared to that observed in the $Co/Si_{1-x}C_x$ system. The ternary top layers remaining after the solid phase reaction of the bilayers with Si were etched in a CF_4/Ar-plasma. CoF_y identified with the help of the Co edge in EELS spectra was found to be of importance during the etch process of $CoSi_2$. Furthermore self assembling of $NiSi_2$ precipitates in a Si(001) matrix was studied. Depending on the parameters of Ni and Si co-deposition in a MBE system a variation of the self assembling behaviour of the $NiSi_2$-precipitates was observed.

FF4.6

IN SITU INVESTIGATION OF THE FORMATION OF NICKEL SILICIDES DURING INTERACTION OF SILICON WITH NICKEL. Boris Bokhonov, Mikhail Korchagin, 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_2Si, b) annealing at temperatures above 600 C is accompanied by the formation and epitaxial growth of the $NiSi_2$ phase. The growth of nickel disilicide crystal phase is accompanied by the formation of dislocations both in the nickel disilicide phase, and in silicon phase. The interaction of the amorphous silicon film with nickel particles at temperatures above 600 leads to the crystallization of several silicide phases: $NiSi_2$, NiSi, Ni_3Si_2. 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 nickel-silicon systems. The irradiation with the beam of accelerated electrons in microscope leads to the increase of the rate of silicide phase formation and to the decrease of the temperature, at which nickel disilicide phase growing epitaxially is formed, at least to 400 C. In our opinion, the observed effect can be due to the formation of radiation defects in the structure of single crystal silicon.

FF4.7

CHARACTERIZATION OF OXYGEN-DOPED V-4%Cr-4%Ti 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-4%Ti 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-h-anneal at 1200°C, sheet specimens were subjected to extended (16h to 43h) 500°C anneals in 5 to 8 $\times$ 10^{-6} torr oxygen, followed by a homogenization vacuum anneal of 100 h at 600°C. Weight gains indicated ~200 to >1400 wppm oxygen doping. Microstructural characterization by transmission electron microscopy (TEM) was performed for correlation with tensile data. Techniques included diffraction contrast analyses of secondary defects, energy-filtered transmission electron microscopy (EFTEM) elemental mapping, and high spatial resolution analytical electron microscopy (AEM) with focussed probes. Following oxygen doping and homogenization, high concentrations of nanoscale clusters on {001} are observed in the matrix with a ~200nm-wide precipitate-free zone (PFZ) at grain boundaries. This PFZ corresponds to a depletion in Ti level, apparently arising from a collector-plate mechanism for the formation of Ti(O,C,N) intergranular precipitates. These precipitates show a wide variability in size and concentration from boundary to boundary. An additional vacuum anneal for 4h at 950°C results in the formation of coarse typically 1-μm-diameter plate precipitates <5nm thick, again on {001}. The detailed microstructural characterization results will be presented and discussed in reference to mechanical properties. Research supported by the Office of Fusion Energy Sciences and at the ORNL SHaRE User Facility by the Division of Materials Sciences and Engineering, U.S. Department of Energy, under contract DE-AC05-00OR22725 with UT-Battelle, LLC.

FF4.8

MICROSTRUCTURAL ANALYSIS OF ULTRAFINE GRAINED MATERIALS PRODUCED BY ECAP. Inyoung Kim, Jongryoul Kim, Dong Hyuk Shin, Hanyang Univ, Dept of Metallurgy and Materials Engineering, Ansan, Kyunggi-Do, KOREA (SOUTH).

Nanocrystalline and ultrafine grained (UFG) materials have attracted much attention in recent years since they exhibit excellent mechanical properties. Of several methods for fabricating bulk UFG materials, equal channel angular pressing (ECAP) is rapidly becoming an established process for inducing grain refinement in metallic materials through simple shear caused by pressing a sample through a die with two intersection channel, equal in cross section. It has been reported that UFG materials produced by the ECAP might have major differences compared with coarse grained materials in fundamental properties including the elastic modulus and the Debye and Curie temperature. These experimental results show that the ECAP has the potential for changing the material properties in a controlled way, for which the deformation mechanism and grain boundary structures have to be understood. In this study, slip systems and grain boundary structures have been analyzed by TEM in order to investigate the mechanism of grain refinement and the effect of grain boundary structures on low carbon steel. In the process of repetitive ECAP, the strain path was controlled by the sample rotation for enhancing the grain refinement. Attention was paid to the structural evolution on the role of the controlled strain path. The mechanism of grain refinement was elucidated through the structural analysis of slip systems in shear bands. HREM images were used for the observation of grain boundaries, especially non-equilibrium boundaries possessing excess boundary energy and long range elastic stress produced by the ECAP.

FF4.9

MICROSTRUCTURE AND PHASE DECOMPOSITION OF QUASICRYSTAL $Zn_{60}Mg_{30}Y_{10}$. Y.L. Cheung, K.C. Chan, Dept of Manufacturing Engineering, The Hong Kong Polytechnic University, Hung Hom, Hong Kong SAR, CHINA; Y.H. Zhu, Instituto de Inverstigaciones en Materiales, Universidad Nacional Autonoma de Mexico, Mexico D.F., MEXICO; Dept of Manufacturing Engineering, The Hong Kong Polytechnic University, Hung Hom, Hong Kong SAR, CHINA.

Microstructure and aging characteristics of a quasicrystal $Zn_{60}Mg_{30}Y_{10}$ alloy was studied using X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) techniques. Typical structures of the icosahedral quasicrystalline phase were characterized of three symmetries: 5-fold, 3-fold and 2-fold, based on which a structure model of this complex quasicrystalline phase was proposed. Fine-dispersed precipitates were found inside the relatively stable quasicrystalline phase during aging. Decomposition of the crystalline phase ($MgZn_2$) was also investigated.

FF4.10

IN-SITU TEM ANNEALING AND STRAINING EXPERIMENTS ON HIGH STRENGTH AND HIGH CONDUCTIVITY CUNIBE ALLOY. Meimei Li, University of Illinois at Urbana-Champaign, Dept of Nuclear, Plasma and Radiological Engineering, Urbana, IL.

High strength and high conductivity Hycon3HP^{TM}CuNiBe showed a rapid reduction in fracture resistance with increasing test temperature, even tested in vacuum. Scanning Electron Microscopy examination on the fracture surfaces indicated that the samples had a mixed mode of intergranular and transgranular fracture tested both at room temperature and elevated temperatures. As the test temperature increases, the percentage of intergranular fracture increases. In-situ TEM annealing and straining experiments were performed on this alloy to investigate the mechanism controlling the flow and fracture behavior of this material. Microstructural analysis of

the CuNiBe alloy shows that both continuous and discontinuous precipitation occur in this alloy. Large lamellar discontinuous precipitates near grain boundaries are suggested to have a 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 at elevated temperatures.

FF4.11
TEM AND LVSEM INVESTIGATIONS FOR THE CHARACTERIZATION OF COMPATIBILIZED POLYMER/ POLYMER INTERFACES. Ines Schwarz, Thorsten Späth, 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 immiscible polymers, the system polyethylene/polypropylene being one of the most commonly used. As adhesion between these non-polar polymers is rather weak, compatibilizers have to be used to increase the strength of adhesive bonding. Usually, the weak interfacial adherence of two immiscible 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 strengths of adhesive joints, a modified T-peel test was applied allowing to measure detaching forces for the untreated as well as for the compatibilized interface within the same sample. To obtain information on the interfaces, multi layer sandwiches comprising films of PE and PP, alternating with layers of compatibilizer, were prepared. Cross-sectional microtome cuts of these sandwiches were etched 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 smoothed and etched sample surfaces were prepared, revealing lamellar details 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' adhesive properties. Mechanical interlocking in μm-scale was clearly illustrated. Additional information on the mechanisms of adhesive 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. Velazquez, J. Reyes and V.M. Castano, Instituto de Fisica, UNAM, Laboratorio de Juriquilla, Queretaro, MEXICO.

An acrylic system consisting of methyl methacrylate and triethylen glycol dimethacrylate undergoes phase separation when the system is synthesized through bulk polymerization using N, N dimethyl p-toluidine at room temperature. The phase separation produce the formation of microdomains with different chemical compositions. The size, shape and morphology of these microdomains have an 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 made easier 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 Micro-Raman spectroscopies complete the microstructural Characterization of the microdomains.

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

Amorphous chalcogenides in contact with silver or copper exhibit a remarkable sensitivity to various forms of radiation. In this study the influence of electron beam irradiation on bi-layers of amorphous chalcogenides and silver or copper has been investigated. A focused electron beam was utilised to produce patterns of nanometre dimensions, such as fine lines or dots in these films. Transmission 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. Preparation parameters such 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 have a higher metal content than the remainder of the films. In addition, the conductivity of line patterns has been investigated.

SESSION FF5: ELECTRONIC AND SEMICONDUCTING MATERIALS

Chair: Eric A. Stach
Wednesday Morning, April 18, 2001
Salon 15 (Marriott)

8:30 AM FF5.1
ACCURACY OF HRTEM GATE OXIDE THICKNESS MEASUREMENTS. John Henry J. Scott and David S. Bright, NIST, Surface and Microanalysis Science Division, Gaithersburg, MD.

The accuracy of high-resolution TEM gate oxide thickness metrology is studied using multislice 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 the true thicknesses of the oxide used 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 condition parameters such as beam voltage, beam tilt, defocus, along-beam thickness, stigmatism, and sample vibration are studied systematically.

8:45 AM *FF5.2
NANOSCALE STUDIES OF STRESS DISTRIBUTIONS, DEFECTS AND MICROSTRUCTURAL DEGRADATION MODES IN SEMICONDUCTOR DEVICES. R. Hull, J. Demarest and D. Mathes, Department of Materials Sci, University of Virginia, VA; K. Schonenberg, IBM, East Fishkill, 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 avenues 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 prime advantage of FIB preparation of TEM specimens 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 characteristic 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.

9:15 AM FF5.3
MEASUREMENT OF LOCAL STRAIN IN THIN ALUMINIUM INTERCONNECTS USING CONVERGENT BEAM ELECTRON DIFFRACTION. Stephan Krämer, Cynthia A. Volkert, Eduard Arzt, Manfred Rühle, Max-Planck-Institut für Metallforschung, Stuttgart,

GERMANY; Joachim Mayer, Gemeinschaftslabor für Elektronenmikroskopie, RWTH Aachen, Aachen, GERMANY.

Energy filtered convergent beam electron diffraction (CBED) was used to measure lattice parameters with high spatial resolution (10-100 nm) in unpassivated aluminium interconnects with widths smaller than 400 nm. By introducing the Hough transform for the detection of the higher order Laue zone (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. As a result the triaxial 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 anisotropy due to the different crystallographic orientations of the grains. It will therefore be discussed whether these inhomogeneities are generated by dislocation strain fields or by local variations in grain boundary or interface structure.

9:30 AM FF5.4
FABRICATION AND DEMONSTRATION OF A WET ELECTROCHEMICAL CELL FOR IN-SITU TEM ELECTROPLATING EXPERIMENTS. Mark J. Williamson, University of Virginia, Department of MS&E, Charlottesville, VA; Frances Ross, S. Jay Chey, IBM TJ Watson Research Center, Yorktown Heights, NY.

Copper electroplating has emerged as the leading means of fabricating advanced interconnect structures in integrated circuits, yet many of the physical processes involved in the nucleation and growth of these layers are not fully understood. Based on the length scales involved with many of these processes, transmission electron microscopy is an obvious candidate for their investigation. Therefore, we have developed an electrolytic wet cell for in-situ transmission electron microscopy experiments in the Hitachi 9000 UHV-TEM at IBM TJ Watson Research Center. The cell consist of a liquid reservoir next to a 100 mm X 100 mm electron transparent region which houses one of the electrodes. The other electrode is placed in the reservoir. When imaging an electrolytic process the electron beam passes through two silicon nitride windows, the electrode and the electrolytic solution, giving a total thickness of about one micron. To aid in imaging the large sample thickness both zero-loss and energy filtered imaging video may be recorded with the aid of a Gatan Imaging Filter. This filter is connected to a Gatan Matscan camera allowing image recording at 12 frames per second. These cell have great potential in allowing for electrolytic and galvanic experimentation within the vacuum environment of the TEM. Currently, we are investigating copper electroplating on both Ti/Au and Ti/TiN/Cu cathodes in order to determine mechanisms of nucleation and growth as well as room temperature grain growth of electrodeposited Cu films. We will present both optical and TEM videos of the Cu deposition showing both growth on the electrode and lateral growth in the plane of the electrode and we will discuss the lateral growth of dendritic Cu and the nucleation and dissolution of Cu grains.

9:45 AM FF5.5
Al-Cu BLANKET FILM MICROSTRUCTURE: A COMPARISON AMONG FIB, TEM and EBSP (BKD) TECHNIQUES. L.M. Gignac, C.E. Murray, K.P. Rodbell, IBM T.J. Watson Research Center, Yorktown Heights, NY; M.A. Gribelyuk, IBM Microelectronics, Hopewell Junction, NY.

The microstructure (local texture, grain size and grain size distribution) was determined for a series of 0.5 μm thick Al-0.5wt.% Cu blanket thin films deposited on Si/SiN_x and Si/phosphosilicate glass (PSG) substrates at various temperatures to induce varying degrees of grain growth. The median grain size of the films studied ranged from 0.5 to 2.5 μm. Three techniques were used to quantify the Al-Cu microstructure. First, a focused ion beam (FIB) system was used to mark each blanket sample to ensure that the same region in each film was analyzed. FIB secondary electron images were taken of the marked regions at six different tilt angles and the grain structures were determined from the ion channeling contrast mechanism in the FIB images. The marked regions were then interrogated using electron backscattered pattern (EBSP) analysis (also known as backscattered Kikuchi diffraction, BKD) from which the grain area, grain area distribution, local grain texture and grain misorientation data were determined. The grain area data from EBSP was compared to that measured using both planview transmission electron microscopy (TEM) and FIB. The results of this comparative study showed that both TEM and FIB analyses obtained similar median grain area values and grain area distributions, but the EBSP analysis found a smaller median grain area value. A detailed analysis of the ESBP technique showed that the grain area distributions were weighted toward smaller grain areas due to scan step limitations, pixel resolution and the accuracy of the tilt correction factor. When these factors were corrected, EBSP 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.

10:30 AM FF5.6
OHMIC CONTACT FORMATION IN COMPOUND SEMI-CONDUCTOR DEVICES. Qianghua Xie, Peter Fejes, Ha Le, Process and Material Characterization Laboratory, Semiconductor Products Sector, Motorola Inc., Mesa, AZ; Ellen Lan, Digital DNA Laboratories, Semiconductor Products Sector, Tempe, AZ.

The increase in wireless communications has created a dramatic demand for high-volume of compound semiconductor based devices. The microstructure of the electrical contacts to the devices can directly impact their contact resistance and thus their microwave properties and power handling capabilities. In this study, we examine the formation of a new type of Ohmic contact, i.e. AuGeNi on a GaAs/In(Ga,Al)P/InGaAs heterostructure, by transmission electron microscope (TEM). The growth of NiGeAs(P) grains is confined by those interfaces leading to an evident lateral grain expansion in GaAs or InGaP. The Au-containing grains selectively locate the InGaP/InGaAs-channel interface. Using nano-probe EDS, the composition of the NiGeAs grains in GaAs is determined to be 50% Ni, 33% As and 17% Ge. In InGaP/InGaAs, the grains has 27% Ni, 29% Ga(In), 4% As(P) and 14% Ge. The Au-containing grains at the InGaP/InGaAs interface, have a composition of 46% Au, 14.6% Ni, 16.4% Ga and 23% As while annealed at 420 °C for 30 sec. Whereas annealed at a higher annealing temperature of 460°C for 60 sec, Au containing grains expand laterally and are enriched by more Au diffusion from the contact. These TEM results can explain the fact that at higher annealing temperature, higher on-resistance of the devices is observed.

10:45 AM *FF5.7
COMPOSITIONAL ANALYSIS BASED ON ELECTRON HOLOGRAPHY AND A CHEMICALLY SENSITIVE REFLECTION. Andreas Rosenauer, University of Karlsruhe, Laboratory for Electron Microscopy, Karlsruhe, GERMANY; Dirk Van Dyck, University of Antwerp, EMAT, Antwerp, BELGIUM; Markus Arzberger and Gerhard Abstreiter, Technical University of Munic, Walter Schottky Institute, Garching, GERMANY.

Thin layers of ternary sphalerite type material like e.g. $Al_xGa_{1-x}As$ and $In_xGa_{1-x}As$ are used for the fabrication of optoelectronic devices like light emitting diodes and laser diodes. Optical and electronic properties of such devices are strongly influenced by the spatial distribution of the composition x. Processes like segregation and diffusion lead to deviations between nominal and real concentration profiles. In this contribution we present a method for compositional analysis of low-dimensional heterostructures. The suggested procedure is based on electron holography and the exploitation of the chemically sensitive (002) reflection that is available in sphalerite type material. We apply an off-axis imaging condition where the specimen is tilted about 4° along the (004) 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 of 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 lens aberrations and that lead to a shift of the spatial information of (000) and (002) reflections are taken into account. The application of the 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 a superlattice period of (4.86 ± 0.03) nm and 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 $R = 0.51 \pm 0.02$.

11:15 AM FF5.8
LATERAL ATOMIC ORDERING IN GaAsSb ON (001)InP. V.Y. Fink, E. Chevalier, O.J. Pitts, 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) $GaAs_{1-x}Sb_x$ films ($0.4 < x < 0.6$), using conventional, plan-view and cross-sectional transmission electron microscopy (TEM. 2.5Å point resolution). The samples were grown by metalorganic vapor phase epitaxy onto oriented InP(001) substrates, at temperatures ranging from 500-620°C, and growth rates of 1.5 Å/s (0.54 μm/hr). Ordering occurs in only one [110] in-plane direction, detected in plan-view via the presence of [110] fringes in bright field images, and (220) streaks

or superlattice spots in corresponding selected area diffraction (SAD) patterns. We observe two types of periodicities with twice or four times the random alloy 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 likely a surface mediated process, 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. This ordering is likely related to variations in carrier mobilities that we have observed in this material. We will be investigating the samples further using a more powerful instrument where we expect that Z-contrast and/or high angle annular dark field imaging, together with standard lattice imaging 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. Murgatroyd, A.G. Norman and G.R. Booker, J.Appl.Phys.67 (1990) 2310.

SESSION FF6: SUPERCONDUCTING AND MAGNETIC MATERIAL

Chair: John E. Bonevich
Wednesday Afternoon, April 18, 2001
Salon 15 (Marriott)

1:30 PM *FF6.1
SOLVING MATERIALS PROBLEMS WITH ENERGY-FILTERING TEM AT HIGH SPATIAL RESOLUTION. Werner Grogger, Kannan M. Krishnan, Lawrence Berkeley National Lab., Mat. Sci. Dept., NCEM, Berkeley, CA; Maria Varela del Arco, Univ. Carlos III 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 highlight 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 $[YBa2Cu3O7]_x/[PrBa2Cu3O7]_5$ (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 Pr 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 can be enhanced by the segregation of Cr to the grain boundaries. It has been reported that the intergranular Cr concentration can reach values high enough to render the alloy locally non-magnetic. This magnetic decoupling is responsible for better recording characteristics (e.g. 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 (ΔM plots) and the signal to noise in the recording process.

2:00 PM FF6.2
ENERGY FILTERED IMAGING IN METALLIC MULTILAYER SYSTEMS. J.E. Bonevich, NIST, MS&E 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 300 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 increases the degree of intermixing with an attendant structural accommodation. Intermixing can also dramatically affect the interfacial stress in multilayered systems. EFI and HRTEM characterization of highly textured {111} Ag/Ni thin films has been employed in conjunction with the measurement of in-plane strain as a function of bilayer thickness. An interface stress of -2.02 /- 0.26 N/m was measured for bilayer thickness greater than 5 nm. While for smaller bilayer thickness, a smaller interface stress may be related to the interdiffusion of several monolayers. These results as well as EFI/HRTEM/TED investigations of Al/Ti multilayered films will be presented.

2:15 PM FF6.3
QUANTITATIVE NANOMETER-RESOLUTION COMPOSITION MAPPING OF SEGREGATION IN Co-BASED THIN-FILM MAGNETIC RECORDING MEDIA. J. Bentley, Oak Ridge National Laboratory, Metals and Ceramics Div, Oak Ridge, TN; J.E. Wittig, Vanderbilt Univ, 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 aspects 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 $Cr-L_{23}$ (575 eV) core-loss intensities in the presence of surface oxide (O K-edge at 532 eV) is an essential component of these procedures. Commonly in media with 12 to 16% Cr, maximum intergranular Cr levels are 24 $\pm$ 5%, and grain interiors may have <5% Cr. Unfortunately, Ta and Pt, which are important additional alloying elements, are not amenable to quantitative elemental mapping by EFTEM, but can be mapped by high-spatial-resolution energy-dispersive X-ray spectrometry (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 to EFTEM. For some advanced media, the distribution of other elements such as boron, is of great interest. Reliable methods for quantitative boron mapping, either by EFTEM or EELS spectrum imaging, require the use of non-standard background subtraction procedures. The tails of the 3d transition metal M edges produce a background at the B K-edge (190 eV) that deviates from the usual inverse power law (AE^{-r}). Log-polynomial background fitting procedures have been shown to yield reliable net B-K core-loss intensities for quantitative composition measurement. Research at the Oak Ridge National Laboratory SHaRE User Facility was sponsored by the Division of Materials Sciences and Engineering, U.S. Department of Energy, under contract DE-AC05-00OR22725 with UT-Battelle, LLC, and through the SHaRE Program under contract DE-AC05-76OR00033 with Oak Ridge Associated Universities.

2:30 PM FF6.4
IN-SITU TEM STUDIES OF THE EVOLUTION OF NANO-SIZED METAL AND OXIDE PRECIPITATES IN A METAL MATRIX. B.J. Kooi, T. Vystavel, S. Mogck, J. Th. M. De Hosson, Dept of Applied Physics, Univ of Groningen, Groningen, The NETHERLANDS.

Nano-sized metal and oxide precipitates are of interest for e.g. dispersion hardening, giant magneto-resistance and basic research of interfacial structures. To this purpose we studied (magnetic) Co, CoFe and CoPt precipitates in a Au matrix and Mn_3O_4 and $ZnMnO_3$ precipitates in a Ag matrix using HRTEM, energy-filtered TEM and nano-probe EDXS 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 ZnMnO3 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 fct CoPt result in markedly different precipitate shapes, orientation relations and interface orientations. These differences turned out to have large effects on the Giant Magnetoresistant properties we measured (fields up to 5 Tesla and temperatures down to10 K). The Co precipitates have truncated octahedral shapes and under conditions where their size is about 4 nm they show a GMR effect typical for super-paramagnetic fluctuations. On the other hand the CoFe precipitates have a plate 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 for multi-layer structures. Interesting about the in-situ reduction of the Mn3O4 and ZnMnO3 precipitates is that we could explain the observed reduction kinetics and Ostwald ripening of the MnO precipitates and show the important effect of the strain developing in the precipitates during reduction on the reduction kinetics. These strains could event prevent the reduction for a longer time.

2:45 PM FF6.5
VALENCE MAPPING OF MANGANESE OXIDE PARTICLES

USING EFTEM AND STEM-BASED SPECTRUM IMAGING. Rhonda M. Stroud, Naval Research Laboratory, Washington, DC; John Henry J. Scott, Surface and Microanalysis Science Division, National Institute of Standards and Technology, Gaithersburg, MD.

The L_3 and L_2 absorption edges of the electron energy-loss spectra of 3d transition metal oxides exhibit peaks, called white lines, corresponding to 2p to 3d transitions of different spin configurations. Barring any change in the spin sub-band populations, the relative intensity of the peaks is a measure of the density of unoccupied states, i.e. the valence or oxidation state of the transition metal. Using either energy filtered transmission electron microscopy (EFTEM) or scanning transmission electron microscopy (STEM)-based spectrum imaging, maps of the change in white line ratio can be obtained with high spatial resolution. We use a five-window method for producing these valence maps, specifically designed to investigate surface layers on particulate samples. We have applied this technique to mapping Mn oxidation states for MnO, Mn_2O_3 and MnO_2 particulate samples. Features that indicate surface oxygen depletion (higher Mn^2 content) appear in the valence maps of some MnO_2 nanoparticles. This technique is expected to have applications in investigating the variation in oxidation state of catalytic and magnetic nanoparticles.

3:30 PM *FF6.6
TOWARDS ACCURATE MEASUREMENTS OF INTERFACIAL CHARGE DISTRIBUTION AND LATTICE DISPLACEMENT USING INTERFEROMETRIC METHODS. Yimei Zhu, Materials Science Division, Brookhaven National Laboratory, Upton, NY.

We report a novel interferometric shadow-imaging diffraction technique to study charge distribution and lattice displacement across planar defects and grain boundaries using a coherent electron source. The technique is based on PArallel Recording of Oscillating Diffraction Intensity of many reflections (PARODI). Unprecedented sensitivity in measurements was achieved by studying electrons scattered near the forward directions for measuring charge while studying those at very large-angles for measuring displacement. The accuracy was significantly improved by quantitative analysis of the interference contrast associated with the defects using fitting and refinement procedures [1]. Applications to Bi/2212 superconductors will be given. Comparison to the measurements both on the potential variation and displacement from the same defects using off-axis electron holography will also be presented.
This work is supported by U.S. Department of Energy, Division of Materials, Office of Basic Energy Science, under Contract No. DE-AC02-98CH10886.
[1] L.Wu, Y.Zhu and J. Tafto, Phys.Rev.Lett. in press (2000).

4:00 PM *FF6.7
QUANTITATIVE ELECTRON DIFFRACTION AND APPLICATIONS TO MATERIALS SCIENCE. J.M. Zuo, Dept. of MS&E and Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, IL.

Recent developments in quantitative electron diffraction make it possible to 1) map the details of the electron distribution in crystals, 2) measure the strain in thin films, and 3) record quantitative electron diffuse scattering. These quantitative electron diffraction techniques complement X-ray and neutron diffraction with the electron sensitivity to the charge distribution and the local structure information obtainable with the small electron probe. Three examples will be given. The first example is the accurate measurement of charge densities in cuprite, Cu2O. By combining accurate electron diffraction measurements of the low order structure factors with the high order X-ray structure factors, we improved the accuracy of experimental charge densities by a factor of 10 or more. This improvement allows us to observe the details of chemical bonding and reveal the shape of d-holes in cuprite. The second example is the accurate measurement of the strain in thin films using nanometer-sized electron probe, By mapping changes in the lattice parameters as a function of probe positions, high-resolution strain filed across interfaces, around defects and nanostructures can be obtained. The third example is the quantitative study of electron diffuse scattering in colossal magnetoresistive manganites. In this case, electron diffraction data from a single crystal domain was combined with X-ray and neutron bond-length measurements for the quantitative determination of nano-clusters near the transition temperature. The advantage of electron diffraction is the strong electron interaction with matter and the small electron probe. Recent developments in electron energy-filter, digital electron detectors and electron diffraction simulation algorithms make it possible to analyse electron diffraction intensity quantitatively. The examples to be presented will demonstrate the advantage of combined electron, X-ray and neutron diffraction analysis for advanced materials.

SESSION FF7: NOVEL INSTRUMENTS AND TECHNIQUES
Chair: Jian-Min Zuo
Thursday Morning, April 19, 2001
Salon 15 (Marriott)

8:45 AM *FF7.1
SURFACE MICROSCOPY WITH SLOW REFLECTED AND EMITTED ELECTRONS. Ernst Bauer, Arizona State University, Tempe, AZ.

(ABSTRACT NOT AVAILABLE)

9:15 AM FF7.2
STEP FLUCTUATIONS ON (011) SURFACES OF REFRACTORY METALS STUDIED BY LEEM. M. Ondřejček, W. Święch, 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 mesoscopic scale 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 $(11\bar{2}0)$ oriented sapphire substrates. Small miscut substrates with various azimuthal orientations were used. Experiments have been performed within the temperature range 1390K 1760K. At lower temperatures Mo surfaces after an appropriate annealing procedure consist of almost parallel trains of monatomic steps [2]. In contrast, steps on Nb (with submonolayer oxygen content) tend to bunch together and form nanofacets [3]. However, at temperatures above 1530K Nb facets separate into fairly straight single steps with the exception of the miscut exactly in the $(0\bar{1}1)$ direction. In both cases, steps are not stationary. Large-scale oscillations of isolated steps have been recorded. The goal of the experiments was to investigate the time and wavelength dependence of the equilibrium step fluctuations as a function of element, temperature and substrate miscut 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.
[1] N.C. Bartelt and R.M. Tromp, Phys. Rev. B **54**, 11731 (1996).
[2] W. Świćech, M. Mundschau and C.P. Flynn, Surf. Sci. **437**, 61 (1999).
[3] C.P. Flynn, W. Świćech, R.S. Appleton and M. Ondřejček, Phys. Rev. B **62**, 2096 (2000).

9:30 AM FF7.3
TOPOGRAPHICAL CONTRAST FROM A PATTERNED SEMICONDUCTOR SUBSTRATE IN LOW ENERGY ELECTRON MICROSCOPY. Hung-Chih Kan, R.J. Phaneuf, Laboratory for Physical Sciences, Department of Physics, and Department of MS&E, 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 pattern-associated corrugation on the sub-micrometer scale. Low energy electron microscopy (LEEM) provides video rate imaging of surfaces at a 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 microscope 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 incident electrons, which produces strong “topographic contrast” in the image.
Work supported by the Laboratory for Physical Sciences and by and NSF-MRSEC

9:45 AM FF7.4
THE SEM MIRROR METHOD: A NEW TOOL TO INVESTIGATE INSULATORS. J. Bigarré, P. Hourquebie, 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 is 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 (typicaly 0.3 KeV) in scanning mode. On account of the negative charge trapped under the surface, 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 seen. A complete mirror experiment consists of measuring the exit gun size versus the scanning potential until the mirror disappears. If the charges are taken as punctual, the electrostatic potential is central and it is simple to calculate the quantity of trapped charges. Recent works try to estimate the trapped charge distribution with more complex analytical or numerical models. This technique has been used to study different insulators like ceramics (Quartz, pure and doped sapphire, alumina, zirconia) and polymers (polyethylene, polypropylene). Some correlation between charge trapping properties and macroscopic behaviors (mechanical or electrical properties) have been established.

10:30 AM *FF7.5
ALCHEMI AND HOLOGRAPHIC ALCHEMI: FINDING FOREIGN ATOM SITES IN MICROCRYSTALS. John Spence, Arizona State University, Tempe, AZ.

The Atom Location by channelling enhanced microanalysis (Alchemi) method uses the electron-beam orientation dependance 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 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, super-alloys and oxides. Recent important advances, such as statistical alchemi and axial 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 summarized, and the challenge of ELS alchemi reviewed. Finally, a new method which allows two-dimensional X-ray alchemi patterns to be interpreted as species-specific holograms of the local environment will be described.
A summary of recent work can be found in Phil Mag A74, p. 57 (1996).

11:00 AM FF7.6
HIGH ANGULAR RESOLUTION ELECTRON CHANNELLING X-RAY SPECTROSCOPY (HARECXS) AS A METHOD OF ESTABLISHING CATION DISPLACEMENT ENERGIES. Nestor J. Zaluzec, 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 alphas/mg or ions/cm^{-2} or) into the standard radiation damage unit of displacements per atom (dpa), requires knowledge of the displacement energies (Ed values) of all the ionic species of the target material. Various titanates have been proposed as host phases for immobilising actinide rich wastes. To date, only the Ed values of oxygen in titanates have been established. The Ed values of cations are estimated from work on other oxides and silicates. High Angular Resolution Electron Channelling X-ray Spectroscopy (HAREXCS) is a new technique for measuring the angular distribution of x-ray emission as a function of orientation. The objective of this study is to establish the minimum heavy ion dose that causes visible change to HARECXS spectra of the <101> row of systematic reflections in perovskite ($CaTiO_3$) samples. From this value we will calculate an (average) cation Ed value for perovskite, as an indicator of the Ed values that should used for other titanates. To date, we have collected data from fully crystalline perovskite and perovskite irradiated to 0.5 and 0.35 times the critical dose for full amorphisation (Dc) of perovskite. The HARECXS signature of perovskite irradiated to 0.35 Dc was significantly different to that of unirradiated perovskite. This data and HARECXS 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 Yeadon, Institute of Matls Research and Engr, and Dept of Matls Sci, Natl Univ of Singapore, SINGAPORE.

The electron microscope is well established in the analysis of thin films and nanostructured materials due to the reasonable 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 according to true UHV design rules, with stable base pressures below 2.10^{-10} 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 paper, a new 'in-situ Materials Development System' is described, located on the campus of the National University of Singapore. The System comprises a JEOL 2000V ultrahigh vacuum transmission electron microscope with in-situ MBE, 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 FF8: CERAMIC MATERIAL
Chair: James Bentley
Thursday Afternoon, April 19, 2001
Salon 15 (Marriott)

1:30 PM FF8.1
INCORPORATION OF LARGE CERIUM IONS INTO THE ALPHA-SIALON STRUCTURE. Fang-Fang Xu, Yoshio Bando, Chang-Meng Wang, Mamoru Mitomo, NIRIM, Tsukuba, JAPAN.

Alpha-sialon is the isostructural derivative based on the alpha-silicon nitride 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 most small rare-earth metals. Large rare-earth metal ions have been considered not to be able to enter the interstices in alpha-sialon structure until several recent sucesses in accomodating large cerium ions (r=0.103nm). This gives rise to questions of the location and distribution of these large cerium ions within the alpha-sialon structure. The Ce-doped alpha-sialon material was prepared in our present work and has been examined by field-emission transmission electron microcope (TEM) equipped with energy dispersive spectroscopy (EDS). TEM observations reveal that almost all the alpha-sialon grains contain high densities of domain boundaries, the type of which could never be discovered in silicon nitride or sialon material doped with small metal ions. The domains are enveloped by some specific faces in this strong-bonded covalent compound, i.e. (0001), 10-11 and the concurrent surface with the matrix crystal on {10-10}. The conventional diffraction contrast analysis suggests that these domains be formed by a single translation of 1/3<10-10> 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 enlargement of interstices by one atomic layer along c-axis at the domain boundary region. This, together with the lattice expansion normal to c-axis, has produced enlarged interstices which become able to accomodate large metal ions like Ce3 .

1:45 PM FF8.2
MORPHOLOGY, MICROSTRUCTURE AND DEFECTS IN FUSED SILICA INDUCED BY HIGH POWER 3w (355 NM) LASER PULSES. Joe Wong[a], D. Haupt[a], J.H. Kinney[a], M. Stevens-Kalceff[b] and A. Stesmans[c], J. Ferriera[a], E. Lindsey[a] and I. Hutcheon. [a]Lawrence Livermore National Laboratory, University of California, Livermore, CA. [b]Department of Applied Physics, University of Technology, Sydney, NSW, AUSTRALIA. [c] Department 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 micro-spectroscopic tools. These include SEM, HRTEM, microprobe analysis, XPS, SIMS and x-ray micro-tomography 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 laser-generated shock waves. The size of the overall crater is dependent on laser fluence, number of pulses, laser irradiation history and environment. In particular, differences in morphology of the damage sites are identified: air vs. vacuum; exit (more severe) surface vs. entrance surface; and regular polish (more severe) vs. super polish surfaces. A compaction 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

stoichiometry of silica in the compaction layer to within ±1.6%. HRTEM indicates the absence of crystalline nano-particles of Si in the compaction layer. Macro- (10-0.1mm) and micro-cracks (200-20nm) are found, however, in the bright field images. The presence of four point defects: NBOHC (non-bridging oxygen hole center), the E', H(1) and ODC II (oxygen deficient center), is also detected and spatially resolved in cathodoluminescence and ESR measurements. These findings are critical to the understanding of laser damage initiation and design of a knowledge-based mitigation process for laser damage growth in NIF (National Ignition Facility) optics.

2:00 PM *FF8.3
UNRAVELING STRUCTURE/PROPERTY RELATIONS AT INTERFACES BY Z-CONTRAST MICROSCOPY, ELECTRON ENERGY LOSS SPECTROSCOPY AND FIRST-PRINCIPLES THEORY. S.J. Pennycook[1,3], G. Duscher[1,3], R. Buczko[4], M. Kim[1,2], N.D. Browning[2] and S.T. Pantelides[1,3]. [1]Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN. [2]Department of Physics, University of Illinois at Chicago, Chicago, IL. [3]Department of Physics and Astronomy, Vanderbilt University, Nashville, TN. [4]Institute of Physics, Polish Academy of Sciences, Warsaw, POLAND.

The combination of atomic-resolution Z-contrast scanning transmission electron microscopy, electron energy loss spectroscopy, and first-principles theory represents a powerful set of tools to link the atomic and electronic structure of interfaces to macroscopic properties. Three case studies will be presented: 1) The origin of electrical barriers at $SrTiO_3$ grain boundaries will be shown to be due to oxygen deficiency. Theory predicts a strong segregation of oxygen vacancies to the grain boundary plane, which is experimentally confirmed by EELS. This leads to excess electrons and band bending. 2) The same effect in the structurally related high temperature superconductor YBCO provides a quantitative explanation of the exponential decrease in grain boundary critical current with misorientation. 3) At the Si/SiO_2 interface, electron energy loss spectroscopy provides a sensitive means to probe the evolution of the band gap from Si into the oxide, with the same spatial resolution as the Z-contrast image. Provided core hole effects are included, theory allows energy loss fine structure to be inverted, allowing electronic structure of the interface to be directly correlated with bonding configurations. Theory also predicts that abrupt interfaces are energetically preferred, and in this case the full SiO_2 band gap is achieved only 0.4 nm within the SiO_2.

2:30 PM FF8.4
STUDY OF INTERFACE MIGRATION IN CERAMIC MATERIALS BY EBSD. J.K. Farrer, N. Ravishankar, University of Minnesota, Dept. of Chemical Engineering and Material Science, University of Minnesota, Minneapolis, MN; J.R. Michael, Sandia National Laboratory, Albuquerque, NM; C.B. Carter, University of Minnesota, Dept. of Chemical Engineering and Material Science, University of Minnesota, Minneapolis, MN.

The sintering process of ceramics generally involves grain-boundary migration (GBM) that is accompanied by mass transport across the interface. In the case of liquid-phase sintering a liquid film may be present at the grain boundaries, which results in enhanced mass transport between the grains. Low-voltage SEM and electron backscatter diffraction (EBSD) was used to study GBM in the presence of a liquid film. In order to control the crystallography of the interface, samples were prepared by hot pressing polycrystalline material to single crystals, of specified orientation, with a glass layer in the boundary. Bicrystals were also prepared in a similar manner using two single crystals, of specified orientation. It was observed that GBM in the controlled samples occurs only when the bounding planes are different and that the direction of migration is not always the same as that predicted by the current theories on GBM. EBSD provides the ability to obtain crystallographic information on a large number of grains and acquire statistical data on the orientation dependence of the direction and rate of GBM. It was also observed that the GBM is spasmodic and leaves behind 'tracks' on the free surface. The tracks are formed as a result of the interaction of the grain-boundary groove with the free surface and indicate prior boundary positions. EBSD has a high enough spatial resolution to study submicron areas near the boundary. EBSD patterns taken from points within the migrated region indicate that there may be small-angle misorientations associated with the tracks on the surface. The study of these misorientations and the statistical data collected from the polycrystalline material provides further insight to the driving force of the boundary migration mechanism.

2:45 PM FF8.5
QUANTITATION OF INTERFACIAL PARAMETERS IN CERAMICS BY EELS SPECTRUM SEPARATION. Hui Gu, State Key Lab of High Performance Ceramics, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai, CHINA.

With the high energy-resolution of a FEG analytical electron microscope, spatial difference technique can be applied to the interface problems, especially in ceramics, more accurately, 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 could guarantee an accurate separation of interfacial 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 approach can reach the best performance 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 nano-meter thick amorphous film is often found at grain boundary. However, this method is not limited to the cases with thin 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 evaluation these boundaries.

3:30 PM *FF8.6
QUANTIFYING OXYGEN VACANCY ORDERING AND SEGREGATION IN PEROVSKITES BY HIGH TEMPERATURE ATOMIC RESOLUTION SCANNING 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 the scanning transmission electron microscope (STEM), i.e. thin specimens and high vacuum (low partial pressure of oxygen), make it the ideal environment to induce oxygen vacancies by in-situ heating. By carefully controlling the thermal drift of the stage and using modern heating holders that are designed for high stability, it is now possible to perform these in-situ experiments while maintaining atomic resolution for Z-contrast imaging and electron energy loss spectroscopy (EELS). This means that the dynamics of oxygen vacancy ordering and segregation can be observed directly on the atomic scale and the effect that it has on the local electronic properties can be quantified. Results will be presented on two perovskite systems. In the case of the $(La,Sr)FeO_3$ system being developed as an ionic conductor, the key to transport is the formation of a highly oxygen deficient material. In-situ results show that above a specific temperature ordered phases begin to form. The energetics 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 boundaries in $SrTiO_3$. Here results indicate that there is a segregation of oxygen vacancies to the boundary plane that results in the formation of a highly electron doped region. Such results are consistent with ab-initio simulations and, as the features of $SrTiO_3$ appear to be prevalent in all perovskites, can explain the widely observed transport properties of many polycrystalline perovkites.

4:00 PM FF8.7
Abstract Withdrawn.

4:15 PM FF8.8
MICROANALYSIS OF POLYTYPOID FUNCTIONAL GRADIENTS FOR JOINING DISSIMILAR CERAMICS:Si^3N^4-Al^2O^3 SYSTEM. Caroline S. Lee, University of California at Berkeley, Dept. of MS&E, Berkeley, CA; Xiao-Feng Zhang, Materials Sciences Division, Lawrence Berkeley Laboratory, Berkeley, CA; Gareth Thomas, Department of MS&E, Berkeley, CA and Materials Sciences Division, Lawrence Berkeley Laboratory, Berkeley, CA.

A unique approach to crack-free joining of heterogeneous ceramics is demonstrated by the use of polytypoids as a Functionally Graded Material (FGM) in the system, Si^3N^4-Al^2O^3. Polytypoids in the Al^2O^3-Si^3N^4 system offer a path to compatibility for heterogeneous ceramics for the following reasons: The CTE of all such Polytypoid is intermediate between that of Si^3N^4 and Al^2O^3, and is approximately chemically compatible with both Si^3N^4 and Al^2O^3. These compounds also have glass-free interfaces, which can give good thermal stability. AlN Polytypoids are planar 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 Si^3N^4 and Al^2O^3 using 12H Polytypoid interlayer has been fabricated without any cracks. 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 500 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 Al^2O^3-rich area and 12H polytypoid was formed at the interface of Si^3N^4-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 PM FF8.9
YTTRIUM SEGREGATION IN HIGH PURITY SUPERPLASTIC Y-TZP: SIGNIFICANCE IN TENSILE CREEP. Siari S. Sosa, Terence G. Langdon, University of Southern California, Departments 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 as 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.