

# SYMPOSIUM EE

## Applications of Synchrotron Radiation Techniques to Materials Science

April 16 – 20, 2001

### Chairs

**Patrick G. Allen**

Glenn T. Seaborg Inst  
Lawrence Livermore Natl Lab  
L-231 Transactinium Sci  
Livermore, CA 94551  
925-423-8955

**Susan M. Mini**

Matls Sci Div  
Argonne Natl Lab  
MSD-223  
Argonne, IL 60439  
630-252-1862

**Dale L. Perry**

Lawrence Berkeley Natl Lab  
MS 70A-11150  
Berkeley, CA 94720  
510-486-4819

**Stuart R. Stock**

School of Materials Sci & Eng  
Georgia Inst of Technology  
GT-MSE  
Atlanta, GA 30332-0245  
404-894-6882

### Symposium Support

†Bede Scientific Incorporated

†Blake Industries, Inc.

Varian Vacuum Technologies

†2001 Spring Exhibitor

Proceedings to be published in both book form and online

(see *ONLINE PUBLICATIONS* at [www.mrs.org](http://www.mrs.org))

as Volume 678

of the Materials Research Society

Symposium Proceedings Series.

\* Invited paper

## TUTORIAL

### ST L/N/EE: ADVANCED TECHNIQUES FOR MATERIALS CHARACTERIZATION AND RELIABILITY TESTING

Monday, April 16, 2001  
1:30 p.m. - 5:00 p.m.  
Salon 10/11 (Marriott)

Advanced microelectronic interconnection structures make use of high-conductivity copper conductors with low dielectric-constant insulators at extremely small dimensions. As a consequence, issues arise in the characterization and reliability of these structures that are not found in the well-used aluminum-silica system. Differences appear in: the microstructure of the copper metallization and the changes induced in it by processing, thermal loading and electromigration; the mechanical characteristics of the surrounding dielectric; and, the resulting interdependence of the reliability of the interconnection structure and the changes in the metal microstructure as constrained by the dielectric. This tutorial will cover these topics, introducing participants to the issues involved and the fundamental reliability concerns for both the metallization and its supporting dielectric encapsulant. Advanced methods for characterizing electromigration behavior (especially that of copper), mechanical properties of dielectrics (especially those of low-k materials), and metallization microstructure (by X-Ray diffraction) will be described.

#### Instructors:

**Du Nguyen**, IBM Microelectronics  
**Hari Rathore**, IBM Microelectronics  
**Robert F. Cook**, University of Minnesota  
**Stuart R. Stock**, Georgia Institute of Technology

#### SESSION EE1: X-RAY DIFFRACTION-STRUCTURES AND TRANSFORMATIONS

Chairs: Joe Wong and Susan M. Mini  
Tuesday Morning, April 17, 2001  
Salon 14 (Marriott)

#### 8:45 AM EE1.1

IN SITU SYNCHROTRON X-RAY DIFFRACTION STUDY OF THE STRUCTURAL TRANSFORMATIONS OF NONSIZED Pd CLUSTERS DURING HYDROGEN CHARGING. **N.M. Jisrawi**, Birzeit University, Birzeit, Palestine Authority; **M. Dornheim**, H. Teichler, Goettingen University, Goettingen, GERMANY; **H. Ehrenberg**, Darmstadt University, GERMANY; **M.T. Reetz**, Max Planck Institute for Kohlenforschung, Muehlheim, GERMANY; **A. Pundt**, Goettingen, GERMANY.

We have studied the structural changes that occur in quasi-free Pd clusters as they absorb hydrogen using in situ x-ray diffraction at the Hamburg synchrotron light source (Hasylab). The clusters were electrochemically prepared by stabilizing them in Octylalcyllammoniumbromide which forms a shell that keeps the metallic particles from coalescing. Transmission electron microscopy studies show that the clusters have an average diameter of about 5 nm. We observe evidence for a cuboctahedral to icosahedral transition that is hydrogen enhanced. These results combined with molecular dynamics simulations using the embedded atom method are used to form a picture of how these clusters form and what their most stable structures are.

#### 9:00 AM EE1.2

FINDING OF LOW SYMMETRY FOR THE  $UPt_3$  CRYSTAL STRUCTURE BY HIGH-ENERGY X-RAY DIFFRACTION. **Donald A. Walko**, J.-I. Hong, T.V. Chandrasekhar Rao, Z. Wawrzak, D.N. Seidman, W.P. Halperin, Northwestern University, Evanston, IL; **M.J. Bedzyk**, Northwestern University, Evanston, IL, and **Argonne National Laboratory**, Argonne, IL; and **D.R. Haefner**, Argonne National Laboratory, Argonne, IL.

The crystal structure of  $UPt_3$  is key to the understanding of the normal and superconducting states in this important heavy fermion compound. We have used high-energy x-ray diffraction and transmission electron diffraction measurements to reinvestigate its crystal structure. Single crystal x-ray diffraction measurements were performed with 75 keV x rays at beamline 5BM-D of DND-CAT at the Advanced Photon Source; high-energy x rays were essential for minimizing absorption in this dense material. The observed diffraction patterns are inconsistent with the traditionally assumed  $P6_3/mmc$  space group. Instead, we have determined that the crystal structure of  $UPt_3$  is trigonal. Deviation from the traditionally assumed hexagonal symmetry is small, corresponding to atomic displacements less than

0.01 Å. Lineshape analysis, performed at beamline IID-C of SRI-CAT, showed significant residual strain due to twinning of trigonal domains. Trigonal structure provides an interpretation for several normal-state properties of  $UPt_3$ , and may be relevant to the existence of the symmetry-breaking field required by most theoretical models of heavy fermion superconductivity.

#### 9:15 AM EE1.3

SOLUTION OF THE  $p(2 \times 2)$  NiO(111) SURFACE STRUCTURE USING DIRECT METHODS. **Natasha Erdman**, Institute for Environmental Catalysis, Department of MS&E, Northwestern University, Evanston, IL; **Oliver Warschkow**, Don E. Ellis, Institute for Environmental Catalysis, Department of Physics and Astronomy, Northwestern University, Evanston, IL; **Laurence D. Marks**, Institute for Environmental Catalysis, Department of MS&E, Northwestern University, Evanston, IL.

In this paper we present a solution for the  $p(2 \times 2)$  NiO (111) surface reconstruction that was obtained using Direct Methods applied to X-ray (synchrotron) diffraction data. The solution was refined with 296 data points and 21 parameters using  $\chi^2$  minimization ( $\chi^2=1.82$ ,  $R=0.17$ ). The surface atoms showed very small relaxation from the bulk interatomic distances (Ni-Ni distances are 2.9 /-0.1Å; Ni-O - 2.0 /-0.1Å). The solution can be characterized by alternating close-packed layers of oxygen and nickel atoms: the top surface layer is nickel terminated with 3/4 of the nickel atoms missing, the next oxygen layer is completely full, and the third, nickel layer, has 1/4 of the nickel atoms missing. The structure is consistent with theoretical predictions of octopolar termination of the surface and exhibits the features observed by previous STM studies. In addition, local density functional calculations have been carried out in this work in order to gain insights into the surface charge distribution and electronic structure of the proposed reconstruction. Calculated partial atomic charges and magnetic moments as well as densities of state are reported. The cation deficient nature of the surface requires the presence of electron holes for charge compensation, which we find mainly located on second layer oxygen atoms.

#### 9:30 AM EE1.4

NEW HIGH PRESSURE FORM OF THE NEGATIVE THERMAL EXPANSION MATERIALS ZIRCONIUM MOLYBDATE AND HAFNIUM MOLYBDATE. **Cora Lind**, Donald G. VanDerveer, Angus P. Wilkinson, Georgia Institute of Technology, School of Chemistry and Biochemistry, Atlanta, GA; **Jiuhua Chen**, Michael T. Vaughan, Donald J. Weidner, Mineral Physics Institute and Center for High Pressure Research, State University of New York, Stony Brook, NY.

Negative thermal expansion (NTE) materials are of considerable scientific and technological interest. Their use in composites may facilitate the control of thermal expansion and allow the attainment of zero expansion. The high-pressure behavior of NTE materials is relevant to their application, as the NTE material will experience compression both during processing and use from the surrounding matrix material when used as a filler in a composite. Phase changes that occur under pressure such as that seen in cubic  $ZrW_2O_8$  (transformation to an orthorhombic phase at 0.21 GPa) are thus undesirable, as the original expansion properties are lost. We have investigated the high-pressure behavior of the NTE materials cubic  $ZrMo_2O_8$  and cubic  $HfMo_2O_8$  in a high-pressure cell using synchrotron radiation for in situ observation. Experiments were carried out at pressures up to 8.6 GPa and at temperatures up to 600°C with both white and monochromatic radiation. The influence of hydrostatic versus non-hydrostatic pressure was investigated. Quasi-hydrostatic experiments on cubic  $AMo_2O_8$  ( $A = Zr, Hf$ ) have shown that the materials undergo a first order phase transition involving an 11% volume decrease between 0.7 and 1.5 GPa. The transition is reversible upon decompression, but shows considerable hysteresis. Under non-hydrostatic conditions, the cubic materials start to amorphize above 0.3 GPa and can be converted to the monoclinic polymorphs when heated under pressure. This is the first time that monoclinic  $HfMo_2O_8$  has been observed. The complete reversibility and high onset pressure of the phase transition in cubic  $AMo_2O_8$  could offer advantages over  $ZrW_2O_8$ . However, the onset of amorphization at pressures as low as 0.3 GPa under non-hydrostatic conditions may place severe limitations on the use of these materials. The different behavior observed under hydrostatic and non-hydrostatic conditions suggests that the stress state of NTE fillers in composite materials needs to be carefully controlled.

#### 10:15 AM EE1.5

STRUCTURE OF CRYSTALLOGRAPHICALLY CHALLENGED MATERIALS BY PROFILE ANALYSIS OF ATOMIC PAIR DISTRIBUTION FUNCTIONS. **V. Petkov** and S.J.L. Billinge, Department of Physics and Astronomy and Center for Fundamental Materials Research, Michigan State University, East Lansing, MI.

Many materials of technological importance are not perfectly

crystalline but contain significant disorder at atomic scale. The powder diffraction spectra of such materials contain a few Bragg peaks and a pronounced diffuse component; this limits the applicability of the usual techniques for structure determination. The problem has its solution in employing the so-called atomic Pair Distribution Functions (PDF) technique. The PDF is a Fourier transform of the powder diffraction spectrum and thus takes into account both the Bragg peaks and the diffuse component of the diffraction data. Consequently, the PDF reflects both the average *long-range* structure and the *short-range* deviations from it. Structure parameters including the unit cell constants and angles, atomic coordinates and thermal factors can be fit to the PDF and the atomic ordering determined. PDF's of high resolution and good statistical accuracy are needed for the technique to succeed. This requires diffraction data to be measured over a wide range of wave vectors,  $Q$ , and can only be achieved by employing synchrotron sources delivering high fluxes of high-energy photons. Details of the profile analysis of atomic PDF's will be discussed and relevant examples given. The usefulness of the techniques will be demonstrated by a case study on the structure of the intercalation compound  $\text{LiMoS}_2$ . The experiments were carried out at the beamline x7A, Brookhaven, and x-rays of energy 30 keV were employed. This rather disordered material was found to possess a triclinic unit cell being a distorted derivative of the hexagonal unit cell of  $\text{MoS}_2$ .

#### 10:30 AM EE1.6

HIGH ENERGY X-RAY POWDER DIFFRACTION STUDIES OF CLATHRATE THERMOELECTRICS. Angus P. Wilkinson, Donald VanDerveer, Cora Lind, Georgia Institute of Technology, School of Chemistry and Biochemistry, Atlanta, GA; R.A. Young, Georgia Institute of Technology, School of Physics, Atlanta, GA; Sarjvit D. Shastri, Peter L. Lee, SRI CAT, Advanced Photon Source, Argonne National Laboratory, IL; George S. Nolas, Marlow Industries, R & D Division, Dallas, TX.

Disorder plays a very important role in determining the properties of clathrate thermoelectrics such as  $\text{Cs}_8\text{Na}_{16}\text{Ge}_{136}$ ,  $\text{Eu}_8\text{Ga}_{16}\text{Ge}_{30}$  and  $\text{Cs}_8\text{Cd}_4\text{Sn}_{42}$ . Dynamic and static disorder of the alkali and rare earth elements inside the cavities of these materials affect their thermal conductivities and their thermoelectric performance. Additionally, the distribution of the elements making up the frameworks of these clathrates influences their band structure and hence their thermoelectric performance. The disorder of the elements inside the clathrate cavities has been examined by variable temperature (20 - 298 K) powder X-ray diffraction using 0.15 Å X-rays. The use of very high photon energies allows the collection of diffraction data that should be largely free from systematic errors, due to absorption and extinction, out to very small minimum d-spacings. With current generation insertion devices at the APS and appropriate optics such data can be obtained in a reasonable time frame. Our analysis of the low temperature diffraction data suggests that the metals located in the clathrate cages are statically disordered for some of the samples examined. The results for  $\text{Cs}_8\text{Na}_{16}\text{Ge}_{136}$  in the range 150 - 298 K are comparable with those obtained by laboratory single crystal diffraction data, giving confidence that high energy powder diffraction can be used when single crystals are not available. Resonant scattering measurements at both the Sn and Cd K-edges have been used along with a 0.15 Å dataset to establish that the cadmium in  $\text{Cs}_8\text{Cd}_4\text{Sn}_{42}$  is not randomly distributed in the framework of this thermoelectric material.

Use of the Advance Photon Source was supported by the U.S. Department of Energy under Contract No. W-31-109-Eng-38.

#### 10:45 AM EE1.7

PHASE DISTRIBUTION AND TRANSFORMATION DYNAMICS IN FUSION WELDS BY IN-SITU DIFFRACTION METHODS USING SYNCHROTRON RADIATION. Joe Wong, J.W. Elmer, T. Ressler and T. Palmer, Lawrence Livermore National Laboratory, University of California, Livermore, CA.

A novel spatially resolved x-ray diffraction (SRXRD) technique utilizing intense synchrotron radiation has been developed to measure phase and microstructural changes down to 200 microns in spatial extent in materials subjected to steep thermal gradients during processing(1-3). This technique has now been applied to map completely the phases and their solid-state transformation in the heat-affected zone (HAZ) of fusion welds in-situ during the welding process. Plain carbon steel (PCS) 1005 is a pseudo-binary Fe-C system containing 0.05 wt% of carbon. As a function of increasing temperature, the system undergoes the following transformations:  $\alpha(\text{bcc}) \rightarrow \gamma(\text{fcc}) \rightarrow \delta(\text{bcc}) \rightarrow \text{liquid}$ . In this paper, the phase distribution and microstructural evolution in the HAZ of PCS welds has been investigated in detail. Nature of the solidification product from the liquid pool, and chemical dynamics associated with the  $\delta \rightarrow \gamma$  transformation in a negative thermal gradient are also elucidated using a time-resolved diffraction mode with 50 ms time resolution. The in-situ phase data will be used to derive the

transformation kinetics in PCS fusion welds in particular, and to test the various kinetic models of phase transformation in fusion welds in general. The phase distribution in the HAZ of a duplex stainless steel will also be discussed.

1. Wong et al., J. Mater. Sc. 32, 1493 (1997).
2. Elmer et al., Met. Mat. Trans. 29A, 2761 (1998).
3. Ressler et al., J. Phys. Chem. B. 102, 10724 (1998).

#### 11:00 AM EE1.8

X-RAY RAPID THERMAL ANNEALING (XRTA). Roy Clarke, Tom O'Donnell, Eric Dufresne, Alejandra Lukaszew, Steve Dierker, University of Michigan, Ann Arbor, MI.

Rapid thermal annealing (RTA) is widely used for electronic materials processing, from the activation of dopants to the healing of lattice defects caused by ion implantation. Here we describe an innovative application of x-ray undulator radiation to simultaneously perform RTA and to probe structural changes that occur *during* annealing. This is made possible by the high power-density of undulator beams ( $\sim 100 \text{ W/mm}^2$ ), combined with their excellent properties as a probe of crystal structure (especially collimation and high-brightness). In some ways XRTA is similar to laser annealing, but there are important differences and unique advantages: first, the penetrating power of x-rays ensures a more uniform and controllable delivery of thermal energy; second, the x-ray energy can be tuned to enhance the coupling into the absorption edge of a particular species, thereby permitting selective annealing of buried layers and nanostructures. In our studies at the MHATT-CAT beam line we have demonstrated XRTA on a number of systems, including bulk materials such as extruded steel wire, and thin film epitaxial materials such as Cu on Silicon (100) wafers. Using a CCD area detector, we are able to monitor the x-ray diffraction pattern in real time as the samples are heated by the undulator x-ray beam. The undulator beam (1st harmonic  $\sim 12 \text{ keV}$ ) heated a 1mm diameter steel wire to  $\sim 1000 \text{ C}$  in a few seconds, and we observed the martensitic transition with 30 msec temporal resolution in both Laue and Bragg geometries. Similarly, in the Cu/Si films we observed an initial improvement in the epitaxial quality, followed by rapid degradation at the onset of silicide formation at  $\sim 150\text{C}$ . The results demonstrate that undulator radiation has interesting and unique possibilities for materials processing, particularly the ability to use the *same* beam for heating and as a structural probe.

Work supported by DoE/BES Grant No. DE-FG02-99ER45743.

#### SESSION EE2: X-RAY DIFFRACTION-STRESS, STRAIN, AND TEXTURE

Chairs: Dale L. Perry and Jianhua Li  
Tuesday Afternoon, April 17, 2001  
Salon 14 (Marriott)

#### 1:30 PM EE2.1

ENERGY DISPERSIVE X-RAY DIFFRACTION PROFILING OF STRESS DISTRIBUTIONS. M. Croft, Physics Dept, Rutgers Univ, Piscataway, NJ; Z. Zhong, J.Z. Hu, National Synchrotron Light Source, Brookhaven National Laboratory, Upton, NY; I. Zakharchenko, T. Tsakalakos, Y. Gulak, Z. Kalman, Ceramics Dept, Rutgers Univ, Piscataway, NJ; R. Holtz, Sadananda, NRL, Washington, DC.

We have developed a general white beam energy dispersive x-ray diffraction (EDXRD) technique for profiling, over large depths, the internal strain fields and have applied to steel and ceramic-coated-steel composite materials. The micro-diffraction volume is defined by collimated incident and diffracted beam paths. The feasibility of this work has been greatly enhanced by our addition development of a total scattered intensity profile (SIP) technique for tomographically profiling these coated-steel composites. Indeed a more powerful generalization of the SIP technique to the separate profiling of the scattered intensity from specific-material diffraction lines will be also be illustrated. The applicability of the SIP method in both transmission and reflection geometries will be discussed. Regarding the EDXRD strain profile method we will discuss in detail its application to a steel specimen: to profile the residual strains from manufacture; to profile the additional strains imposed by cantilever spring stressing; and to profile of the new residual strain distribution after releasing the cantilever stress. The initial strain profile is seen to be interior-compressive and exterior-tensile, typical of the manufacturing process. The strain distribution in the loaded cantilever case is seen to be a superposition of a linear elastic strain (in excellent agreement with theory), and the internal residual strain field. In both the cantilever-strained and post-strain cases the presence of a plastic deformation zone introduced on the tensile-strained side of the cantilever is clearly discernable. Additional

residual strain profiles in ceramic-coated-steel composites before and after fatigue will also be introduced.

Work Supported by ONR No. N000149910424-99PR04801-00.

### 1:45 PM \*EE2.2

X-RAY ANALYSIS OF SPONTANEOUS LATERAL COMPOSITION MODULATION IN  $(\text{InAs})_n/(\text{AlAs})_m$  SHORT-PERIOD SUPERLATTICES. J.H. Li, Z. Zhong, J. Kulik, S.C. Moss, Univ of Houston, Dept of Physics, Houston, TX; V. Holy, Masaryk Univ, Dept of Solid State Physics, Brno, CZECH; A.G. Norman, A. Mascarenhas, National Renewable Energy Laboratory, Golden, CO; J.L. Reno, D.M. Follstaedt, Sandia National Laboratories, Albuquerque, NM.

Spontaneous lateral composition modulation in III-V semiconductor alloy films has recently been realized by growing short-period superlattices consisting of sub-layers of atomic layer thick, such as  $(\text{InAs})_n/(\text{AlAs})_m$ . The morphology of the modulated structure has been demonstrated by TEM and AFM investigations, which suggested that the composition modulation is accompanied by a strain modulation that perforce follows the composition profile. However, a quantitative measure of the modulation in terms of either strain or composition has so far not been addressed. In this work, by choosing specific x-ray diffraction vectors having a large component closely parallel to the modulation direction, which, though may not be accessible in a conventional coplanar diffraction geometry, can be achieved by introducing an inclined, non-coplanar diffraction geometry, we are able to observe a number of lateral satellite peaks around the zero-order superlattice peak. A structural model incorporating both composition and strain enables us to simulate the x-ray intensities of the lateral satellites. Our method, therefore, permits quantitative evaluation of the composition amplitude.

### 2:15 PM EE2.3

SYNCHROTRON X-RAY DIFFRACTION MEASUREMENT OF INTERNAL PHASE STRAINS IN UNIAXIALLY LOADED BULK METALLIC GLASS COMPOSITES. Dorian K. Balch, Northwestern University, Department of MS&E, Evanston, IL; Ersan Ustundag, California Institute of Technology, Department of MS&E, Pasadena, CA; David C. Dunand, Northwestern University, Department of MS&E, Evanston, IL.

Bulk metallic glasses have exceptionally high strengths, but fail catastrophically in tension due to shear band formation. Addition of a reinforcing second phase improves the tensile properties both by inhibiting shear band movement and by load transfer to the stiffer reinforcement. Bulk metallic glass composites were examined at the Advanced Photon Source, Argonne National Laboratory by in-situ transmission X-ray diffraction during uniaxial tensile testing. Amorphous matrix material with a nominal composition of  $\text{Zr}_{157}\text{Nb}_5\text{Al}_{10}\text{Cu}_{15.4}\text{Ni}_{12.6}$  was reinforced with 5 vol% tungsten, 10 vol% tungsten, and 5 vol% tantalum particles of  $\sim 15$  micron diameter. During testing the distorted  $\{110\}$  Debye-Scherrer cones for tungsten and tantalum were captured using a two-dimensional detector at various stresses during loading and unloading. Analysis of the elliptical rings provided particle strain data in directions parallel and perpendicular to the loading axis. Use of an iron powder calibration standard ensured that strain measurements were robust against movement of the sample and fluctuations in synchrotron x-ray wavelength. The tungsten-reinforced composites were loaded to 1000 MPa, unloaded, and reloaded to fracture at 1660 MPa, corresponding to an increase in UTS of 38% relative to the unreinforced matrix. The tantalum-reinforced composite was loaded to 1000 MPa, unloaded, reloaded to 1200 MPa, unloaded, and finally reloaded to fracture at 1585 MPa. The elastic portions of the unloading and reloading stress-strain curves have the same slope as the initial loading curves, indicative of good bonding between matrix and particle. This is confirmed by the fact that lattice strain data are in very good agreement with Eshelby predictions of stress-strain behavior. Yielding of the tungsten and tantalum particles was observed by a decrease in the load transfer efficiency determined through lattice strain measurements. Yielding occurred at the stresses predicted by the von Mises yield criterion.

### 2:30 PM EE2.4

RESIDUAL STRESSES IN SILICON NITRIDE BASED COMPOSITES USING SYNCHROTRON RADIATION SOURCE. Myungae Lee, Yanan Xiao, Dale E. Wittmer, Southern Illinois Univ, Dept of Mechanical Engineering and Energy Processes, Carbondale, IL; Susan M. Mini, Northern Illinois Univ, Dept of Physics, DeKalb, IL; Tim Graber, The Center for Advanced Radiation Sources, The Univ of Chicago, Argonne, IL.

A  $\text{Si}_3\text{N}_4$  baseline composition, containing 3 wt.%  $\text{Al}_2\text{O}_3$  and 9 wt.%  $\text{Y}_2\text{O}_3$ , and  $\text{Si}_3\text{N}_4$ -TiN composites, containing additional 5 wt.% TiN particulates, were investigated. The baseline  $\text{Si}_3\text{N}_4$  and  $\text{Si}_3\text{N}_4$ -TiN composites were processed by turbomilling, pressure casting, and isopressing. They were then continuously sintered to full density,

under a pressureless, flowing nitrogen atmosphere. The flexural strength, fracture toughness, and residual stress were measured for as-machined samples and following quenching in water from 1000°C, 1100°C, and 1200°C. To measure the residual strains (stresses) in the silicon nitride based composites, synchrotron based x-ray diffraction was employed on the BESSRC beamline at the APS at Argonne National Laboratory. The application of synchrotron radiation diffraction for stress analysis opens the possibility to investigate ceramic materials, due to its distinct properties, including: high intensity, broad spectral range, and high collimation. The residual stresses for both the baseline  $\text{Si}_3\text{N}_4$  and the  $\text{Si}_3\text{N}_4$ -TiN composites were determined from the (441) and the (531) reflections, obtained by applying the three-dimensional  $2\theta\text{-sin}^2\Psi$  method. This allowed one to distinguish both the transverse and the longitudinal residual stresses for the near surface regions. In both the baseline  $\text{Si}_3\text{N}_4$  and the  $\text{Si}_3\text{N}_4$ -TiN composites, after thermal shocking, the compressive residual stresses were developed in both directions parallel and perpendicular to the surface. The average residual stresses in the transverse direction were much higher than in the longitudinal direction. The measured residual stresses were compared with the flexural strength and fracture toughness results to determine the effects of residual stress and thermal shocking on the strength and toughness of each material. The results suggested that there should be a maximum thermal shock temperature within the range of 1000°C to 1100°C for improved fracture toughness for both the baseline  $\text{Si}_3\text{N}_4$  and the  $\text{Si}_3\text{N}_4$ -TiN composites. Also, the addition of the TiN appears to improve both the high-temperature strength and toughness of the baseline composition.

### 3:15 PM EE2.5

HIGH RESOLUTION X-RAY CHARACTERIZATION OF TL-2212 SUPERCONDUCTING THIN FILMS. M.J. Daniels, University of Michigan, Dept of MS&E, Ann Arbor MI; J.C. Bilello, University of Michigan, Dept of MS&E, Ann Arbor MI; D. Hyland, Dept of Engineering Science, Oxford University; D. Dew-Hughes, Dept of Engineering Science, Oxford University; C.R.M Grovenor, Dept of Materials, Oxford University.

Thallium based high temperature superconducting films were grown on  $\text{LaAlO}_3$  (LAO) and MgO substrates by thalliation of precursor films by reaction with  $\text{Tl}_2\text{O}$ . High resolution strain measurements and topographic studies were performed using the synchrotron at Stanford Synchrotron Radiation Laboratory. From these results, we have reached preliminary conclusions regarding the effect of film strain and substrate twin spacing on the superconducting properties of Tl-2212 films on LAO and MgO substrates. Rocking curve results show a definite correlation between film strain and Q. The relative strain in samples displaying  $Q > 10^5$  at 5.55GHz (at 50K) is about half that of samples with  $Q < 10^4$  at 5.55GHz (at 50K). Examination of samples where  $Q < 10^4$  at 5.55GHz (at 50K) by SEM also shows localized microstructure defects that may offer a local strain-relief mechanism. White beam x-ray topographic analysis was used to quantitatively measure the degree of twinning in the substrate. No direct link between the Q values and the number of twins in the substrate was noted, however, there was a correlation between Q and twin distribution in the substrate. The results will discuss the relationship between the measured Q values of the microwave cavity and the strain state, microstructure and defect morphology in the superconducting film/substrate couple.

### 3:30 PM EE2.6

SYNCHROTRON X-RAY ANALYSIS OF PHASES AND TEXTURE IN COLD-WORKED SHAPE-MEMORY NiTi WIRES. Andreas Schuster, Heinz Voggenreiter, EADS, Corporate Research Center, Munich, GERMANY; Dorian K. Balch, David C. Dunand, Northwestern University, Dept. of MS&E, Evanston IL.

A series of martensitic, near-equiatomic NiTi shape-memory alloy wires with 0.8 mm diameter were prestrained from 1 to 40% in steps of 1% up to stresses of 920 MPa. The stress-strain curve showed an initial elastic regime, followed by a 6% strain plateau where deformation takes place by detwinning. At higher stresses, another linear region occurs where the detwinned martensite deforms elastically, followed by a plastic region where deformation occurs by slip of dislocations. The unloading portion of the stress-strain curve exhibited recovery of the elastic strains; the detwinning strain still present after unloading could be recovered by heating the material to its high-temperature austenitic phase (shape-memory effect). The deformed, unheated wires were exposed at the Advanced Photon Source (Argonne National Laboratory) to a monochromatic, parallel beam of high-energy x-rays oriented perpendicular to the wire axis. The transmitted low-index diffraction rings of the martensite in different states of twinning were recorded with a high-resolution two-dimensional detector. This geometry is quite similar to that found in a transmission electron microscope and gives information about the bulk of the wire, rather than surface information as in traditional x-ray strain analysis. Texture evolution linked with the detwinning is

addressed, and the results are correlated to the macroscopic stress-strain curve as well as thermal analysis (heating and cooling) experiments carried out on deformed samples.

**3:45 PM EE2.7**

**A SYNCHROTRON X-RAY STUDY OF TEXTURE INDUCED BY APPLICATION OF MAGNETIC FIELDS DURING PHASE-TRANSFORMATIONS IN SHAPE-MEMORY  $\text{Ni}_2\text{MnGa}$ .** S. Yilmaz, Dept of MS&E, Northwestern University, Evanston, IL; R. Vaidyanathan; R.C. O'Handley, Dept of MS&E, MIT, Cambridge, MA; D.C. Dunand, Dept of MS&E, Northwestern University, Evanston, IL.

Ni-Mn-Ga alloys can exhibit a thermoelastic phase transformation near room temperature, which is associated with the shape-memory effect (i.e., temperature-induced strain recovery after twinning) or superelasticity (i.e., strain recovery after a stress-induced phase transformation). Furthermore, because Ni-Mn-Ga is ferromagnetic, there is considerable scientific and engineering interest in inducing reversible twinning by applying external magnetic fields. Magnetically-induced twinning strains as high as 6.1% have been reported in single-crystal  $\text{Ni}_2\text{MnGa}$ . However, the magnetically-induced strains reported in polycrystalline  $\text{Ni}_2\text{MnGa}$  are considerably lower. This work uses a synchrotron X-ray transmission technique to investigate texture induced by applying magnetic fields during the phase transformation in polycrystalline  $\text{Ni}_2\text{MnGa}$ . Synchrotron X-ray radiation is ideally suited for such investigations since the measurements are representative of twinning in the bulk, in contrast with measurements from conventional X-ray sources that represent surface measurements affected by surface relaxation. Magnetic texturing of polycrystalline  $\text{Ni}_2\text{MnGa}$  by cooling through the phase-transformation in the presence of a magnetic field has potential to lead to polycrystalline materials with more compatible field-induced strains and hence increased twin boundary mobility upon application of a magnetic and/or stress field.

**4:00 PM EE2.8**

**TEXTURE ANALYSIS WITH HIGH-ENERGY SYNCHROTRON RADIATION.** Leszek Wcislak, Jochen Schneider, HASYLAB at DESY, Hamburg, GERMANY; Helmut Klein, Univ of Gottingen, Dept of Crystallography, Gottingen, GERMANY; Hans-Joachim Bunge, Technical Univ of Clausthal, Dept of Physics, Clausthal, GERMANY.

The large penetration power (mm - cm) of high-energy X-rays photons in the range (60 - 300 keV) in matter (even in medium-to-high Z materials) opens new interesting possibilities of structural analyses in polycrystalline materials. Optimization of the beamline parameters (photon energy and flux, beam focusing) gives possibilities for performing structure studies within the bulk of the material. It becomes possible to measure non-destructively the fundamental microstructural parameters related with matter in polycrystalline, polyphase states including the number or volume fraction of constitutive phases, the size, shape and arrangement of several phases and grains as well as the crystallographic orientation of the grains within each phase. This allows the quantitative determination of preferred crystallites orientation (texture) in the material and the prediction of its macroscopic physical properties such as deformability, magnetization or superconductivity. Knowing and influencing the preferred orientation of crystallites, (texture tailoring), materials with particular type of anisotropy and required physical or technological properties can be designed and fabricated. X-ray diffraction experiments at high photon energies (short wavelengths) are characterized by relatively small Bragg angles of the order of only a few degrees and the use of synchrotron radiation gives high intensities in the diffraction signal. The use of two-dimensional detectors is of interest for simultaneous registration of many diffraction lines and thus shortening the measuring time. The spatial resolution of the used detector (online image plate) is about 100  $\mu\text{m}$  and enables an angular resolution of the measurement of 0.01 - 0.1°. The area detector data file thus allows the application of more sophisticated mathematical methods for the processing of diffraction patterns (including powerful profile analysis) resulting in relevant texture information. Chosen examples of texture measurements in various materials (metals, ceramics, composites) are presented and discussed, both method advantages and limitations are highlighted.

**SESSION EE3: MICROTOMOGRAPHY AND MICRODIFFRACTION**

Chairs: Stuart R. Stock and Patrick G. Allen  
Wednesday Morning, April 18, 2001  
Salon 14 (Marriott)

**8:30 AM \*EE3.1**

**GRAIN EVOLUTION DURING PROCESSING AS STUDIED BY**

**3-DIMENSIONAL X-RAY DIFFRACTION.** Henning Friis Poulsen, Materials Research Department, Riso Nat. Lab., DENMARK.

We have developed methods and software for fast and non-destructive characterization of the individual grains inside bulk materials (powders or polycrystals). The methods are based on diffraction with hard x-rays ( $E > 50 \text{ keV}$ ), enabling 3D studies within millimeter - centimeter thick specimens. The position, volume, orientation and elastic strain of 10-100 grains can be determined simultaneously. Moreover, for coarse-grained materials the topography of the grain boundaries can be mapped. The methods have been implemented at the 3DXRD microscope at the Materials Science Beamline at the ESRF synchrotron. Following a brief overview of the technique, focus is on a presentation of in-situ results for processing of pure metals. During recrystallization of deformed specimens several hundreds of emerging grains have been characterized with respect to nucleation (nucleation rates, incubation periods, clustering) and grain growth (fluctuations, kinetics as function of orientation). During tensile deformation grain rotations have been determined in a set of embedded grains, providing first data for direct test of polycrystal deformation models. Likewise, the evolution of strain has been followed as function of load. At the end first results from studies of ceramic powders, dislocation structures and the combination with absorption contrast tomography will be summarized.

**9:00 AM EE3.2**

**MESOTEXTURE IN THREE ALUMINUM ALLOYS.** K. Ignatiev, S.R. Stock, Georgia Inst Tech, School of MS&E, Atlanta, GA; Z.U. Rek, Stanford Synchrotron Radiation Lab, SLAC, Stanford, CA.

Samples from the center of plates of AA 2090 T8E41, AA 8090 T8151 and AA 7055 T7751 have been examined with transmission x-ray microbeam diffraction using polychromatic bending magnet radiation. These materials have quite similar macrotexture (sample average texture), very different fatigue properties for identically oriented samples and quite different fatigue crack growth rates. The extremely low crack growth rates observed in AA 2090 were previously tied to the near-single crystal mesotexture in these samples, and the present paper addresses the question of whether such mesotexture is important microstructural feature in samples of other alloys or whether large amounts of near-single crystal mesotexture are an unusual result obtained from the specific processing path and composition for AA2090. These results are particularly important for improved understanding of fatigue crack closure mechanisms.

**9:15 AM EE3.3**

**X-RAY MICRODIFFRACTION AND MICROFLUORESCENCE WITH WHITE-BEAM SYNCHROTRON RADIATION.** G.S. Cargill, III, Lehigh Univ., Dept. of MS&E, Bethlehem, PA.

This paper describes equipment and procedures developed for spatially resolved measurements of strain using x-ray microdiffraction and of composition using x-ray microfluorescence with white-beam synchrotron radiation. Measurements for examining single grains in polycrystals and for averaging over many grains will be described. These measurements have been made with 5-10  $\mu\text{m}$  spatial resolution and  $10^{-4}$  strain resolution. Examples of real-time measurements of strain and composition changes during electromigration in passivated Al and Al(Cu) conductor lines will be used to demonstrate the capabilities of these techniques. Parts of this work have been carried out in collaboration with P.C. Wang, H.K. Kao, K.J. Hwang, A.C. Ho and I.C. Noyan, with support from NSF.

**9:30 AM \*EE3.4**

**X-RAY MICROBEAMS FOR 3-D MESOSCALE MATERIALS INVESTIGATIONS.** B.C. Larson, Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN.

Polychromatic x-ray microbeam techniques exploiting the brilliance of third-generation synchrotrons have been developed for 3-D investigations of materials on mesoscopic length scales of tenths-to-hundreds of microns. Elliptically-figured Kirkpatrick-Baez mirrors are used to focus white x-ray beams to  $\sim 0.5$  micron diameter, and new diffracted beam triangulation methods have been developed to obtain measurements of the local structure, orientation, and full stress/strain tensor of single crystal and polycrystalline materials with micron depth resolution. These capabilities provide new opportunities for non-destructive microstructural investigations of materials ranging from thin-films to bulk samples. The advantages of using polychromatic Laue diffraction for microstructure studies will be considered in connection with a discussion of the measurement and analysis techniques developed for automatic extraction of 3-D spatially resolved information. The power of the techniques developed will be demonstrated by micron resolution measurements of the stress/strain tensor in elastically strained Si, and the range of mesoscale materials physics investigations that can be addressed using

these techniques will be discussed.

Research sponsored by Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U.S. Department of Energy under contract DE-AC05-00OR22725; MHATT-CAT is operated by the University of Michigan, Lucent Technologies, and Howard University; the operation of the APS is sponsored by the DOE.

#### 10:30 AM \*EE3.5

NEW DEVELOPMENTS IN PHASE-CONTRAST MICRO-TOMOGRAPHY. Felix Beckmann, Hamburger Synchrotron Strahlungslabor HASYLAB at Deutsches Elektronen-Synchrotron DESY, Hamburg, GERMANY; Ulrich Bonse, Institute of Physics, University of Dortmund, Dortmund, GERMANY.

Phase-contrast microtomography became a valuable tool for the 3-dim. investigation of samples mainly consisting of light elements. The method was applied to biological samples showing the advantage compared to absorption-contrast microtomography. For the investigation of larger samples and samples consisting of absorbing elements a special manufactured X-ray interferometer was developed. First results using multiple-beam interferometry to perform phase-contrast microtomography of large samples will be presented. Also the feasibility using high-energy phase-contrast microtomography to investigate more absorbing samples will be shown.

#### 11:00 AM EE3.6

COMPARISON OF CRACK GEOMETRY DETERMINED WITH PHASE CONTRAST RADIOGRAPHY AND WITH MICRO-TOMOGRAPHY. S.R. Stock, Georgia Inst Technology, School of MS&E, Atlanta, GA; W.-K. Lee, K. Fezzaa, Advanced Photon Source, Argonne National Lab, User Program Div, IL; G.R. Davis, J.C. Elliott, Queen Mary and Westfield College, Dental Biophysics, London, UNITED KINGDOM.

X-ray microtomography of three-dimensional spatial distribution of crack opening as a function of applied load has helped clarify important processes of roughness-induced fatigue crack closure. Fracture mechanics dictates sample geometries which limit the crack opening sensitivity that can be obtained with microtomography, and there is a real need to be able to quantify smaller openings. Phase contrast imaging with synchrotron radiation may provide the greater sensitivity needed, and this paper compares results of phase contrast radiography and x-ray microtomography of a sample of AA 2090 containing a very non-planar crack.

#### 11:15 AM \*EE3.7

ENERGY-TUNABLE X-RAY DIFFRACTION IN POLY-CRYSTALLINE MATERIALS: A LOOK AT MICROSTRUCTURE IN SEASHELLS. Emil Zolotoyabko, Technion, Dept of Materials Engineering, Haifa, ISRAEL; John Quintana, Northwestern University, DND-CAT Research Center, APS/ANL, Argonne, IL.

Conventional x-ray diffraction at fixed energy encounters serious difficulties in deriving depth-resolved structural information in a wide and very important class of inhomogeneous polycrystalline materials. This problem is solved by means of a newly developed technique which is based on the precise adjusting the energy of synchrotron radiation over a wide range between a few keV and hundred keV. By accurate varying the x-ray energy the structural information can be obtained with a 10 nm depth resolution. This approach affords a non-destructive three-dimensional (3D) diffraction mapping of polycrystalline structures. Application of this technique to seashells allowed us to obtain the 3D-maps of preferred orientation in the nacre layer. We found remarkable oscillations in the degree of preferred orientation across the shells, which indicate the annual (seasonal) variations of mollusk activity in preparing the bio-mineral template for the oriented crystal growth on top of it. Measuring diffraction profiles at different energies we were able to extract important microstructural parameters (strain state and grain size), as a function of depth. This analysis showed that the younger nacre layer, adjacent to the mollusk mantle, is under compressive stress, which prevents crack propagation. Older nacre layers are under tensile stresses, which explains the shell aging process in terms of the accumulation of cracks and other crystal imperfections. The developed technique provides a global non-destructive view of polycrystalline structures on a micro and sub-micrometer scale. It can be used to characterize a very broad spectrum of laminated, structural and composite materials.

#### 11:45 AM EE3.8

STRUCTURAL INVESTIGATIONS ON CARBON FIBERS AND CARBON/CARBON COMPOSITES BY MEANS OF MICROBEAM DIFFRACTION AND MICRO TOMOGRAPHY. Oskar Paris, Univ of Leoben, Metal Physics Inst and Austrian Academy of Sciences, Erich Schmid Inst, Leoben, AUSTRIA; Herwig Peterlik, Dieter Loidl, Univ of Vienna, Materials Physics Inst, Vienna, AUSTRIA; Christoph Rau, European Synchrotron Radiation Facility, Grenoble, FRANCE;

Martin Müller, Univ of Kiel, Inst for Experimental and Applied Physics, Kiel, GERMANY.

Carbon fiber reinforced carbon composites (C/C) are the most promising material for aerospace applications due to their high specific strength (strength to density ratio), which is maintained up to temperatures more than 2000°C. For the extraordinary mechanical properties of the composites at high temperatures, fiber and matrix as well as their interface are responsible. Already the fibers themselves, often designated as “nanocomposites”, are known to exhibit a complex internal structure. At a higher level, C/C composites are characterized by the structure of the fiber/matrix interface and by pores and microcracks within the brittle matrix. Therefore, structural investigations covering several hierarchical levels are required to understand the complex relationship between structure and mechanical properties of C/C. Synchrotron radiation from third generation sources offers unique possibilities to study the structure of complex, hierarchically structured materials. On the one hand, microbeam diffraction ( $\mu$ -XRD) and microbeam small-angle scattering ( $\mu$ -SAXS) allows to get structural information on the micrometer and the nanometer level, simultaneously [1,2]. On the other hand, microtomography using highly coherent, hard X-rays provides three-dimensional bulk information with a resolution down to the sub-micrometer regime. In the present paper we present recent experiments on carbon fibers and on C/C using these new synchrotron radiation techniques. Structural parameters of single carbon fibers, such as axial and cross-sectional texture as well as pore sizes, -shapes and -orientation distributions were investigated by  $\mu$ -XRD and  $\mu$ -SAXS. Moreover, micro-tomography was used to study the three-dimensional distribution of micro-cracks in bi-directionally woven C/C as a function of graphitization temperature and external stress. We will demonstrate the applicability of the techniques to these complex composite materials, discuss their advantages compared to other methods and make some suggestions about future possibilities and improvements.

[1] O. Paris et al., Cell. Mol. Biol. 46(5), 993-1004 (2000).

[2] O. Paris et al., J. Appl. Cryst. 33, 695-699 (2000).

#### SESSION EE4: X-RAY MICROSCOPY AND FLOURESCENCE

Chairs: Angus P. Wilkinson and Stuart R. Stock  
Wednesday Afternoon, April 18, 2001  
Salon 14 (Marriott)

#### 1:45 PM EE4.1

APPLICATIONS OF FULL-FIELD X-RAY MICROSCOPY FOR HIGH SPATIAL RESOLUTION MAGNETIC IMAGING. Gregory Denbeaux, Weilun Chao, Mark Le Gros, Angelic Pearson, Gerd Schneider, Ctr for X-ray Optics, Lawrence Berkeley Natl Laboratory, Berkeley, CA; Peter Fischer, Experimental Physics IV, Univ Wuerzburg, Wuerzburg, GERMANY; Greg Kusinski, Materials Sci Dept, Lawrence Berkeley Natl Laboratory, Berkeley, CA.

The XM-1 soft x-ray microscopy, located at the Advanced Light Source at Lawrence Berkeley National Laboratory has recently been established as a tool for high-resolution imaging of magnetic domains. It is a “conventional” full-field transmission microscope which is able to achieve a resolution of 25 nm using high-precision zone plates. It uses off-axis bend magnet radiation to illuminate samples with elliptically polarized light. When the illumination energy is tuned to absorption edges of specific elements, it can be used as an element-specific probe of magnetism on a 25 nm scale with a contrast provided by magnetic circular dichroism. The illumination energy can be tuned between 250-850 eV. This allows imaging of specific elements including chromium, iron, and cobalt. The spectral resolution has been shown to be  $E/dE=500-700$ . This spectral resolution allows a high sensitivity so that magnetization has been imaged within layers as thin as 3 nm. Since this is a photon based magnetic microscopy, fields can be applied to the samples even during imaging without affecting the spatial resolution. Recent magnetic imaging results will be shown along with results in Biology and Environmental Science.

#### 2:00 PM \*EE4.2

SOFT X-RAY SPECTROMICROSCOPY: QUANTITATIVE CHEMICAL ANALYSIS AT HIGH SPATIAL RESOLUTION. Adam P. Hitchcock, Cynthia Morin, Tolek Tyliczszak, Ivo Koprinarov, Hiromi Ikeura Sekiguchi, Brockhouse Institute for Materials Research, McMaster University, Hamilton, ON, CANADA.

Quantitative chemical analyses of laterally and vertically structured polymeric systems are being performed with sub-100 nm spatial resolution using synchrotron-based scanning transmission x-ray microscopy (STXM) and photoelectron emission microscopy (PEEM) at the Advanced Light Source, Berkeley, CA. Contrast from near edge X-ray absorption (NEXAFS) features provides sensitive differentiation

of species which have similar elemental composition but are chemically distinct. The experimental techniques will be presented and the capabilities will be illustrated by brief reports on several fundamental and applied studies. Examples include: phase segregation in polyurethanes and polymer blends, nano-structured polyurea capsules, water filtration membranes, self-organization of confined polymer films, and protein adsorption on engineered polymeric biomaterials. The presentation will emphasize the capability of adapting soft X-ray spectromicroscopy to a wide variety of problems, from wet systems, to submonolayer surface analysis, to in situ material transformations. Novel methods for converting image and spectral information to quantitative component maps will be described. The Advanced Light Source is supported by DoE under contract DE-AC03-76SF00098. Research is supported by NSERC (Canada).

#### 2:30 PM EE4.3

**SOFT X-RAY SPECTROMICROSCOPY OF THIN FILM POLYMER BLENDS.** C. Morin<sup>1</sup>, A.P. Hitchcock<sup>1</sup>, T. Tyllizak<sup>1</sup>, H. Ikeura Sekiguchi<sup>1</sup>, R. Cornelius<sup>2</sup>, J.L. Brash<sup>2</sup>, A. Scholl<sup>3</sup>, F. Nolting<sup>3</sup>, G. Appel<sup>4</sup>, K. Kaznachejev<sup>4</sup>, H. Ade<sup>4</sup>. <sup>1</sup>Brockhouse Inst. for Matls Res., McMaster Univ., Hamilton, ON, CANADA. <sup>2</sup>Pathology, Chem. Eng., McMaster University, Hamilton, ON, CANADA. <sup>3</sup>Advanced Light Source, Berkeley Lab, Berkeley, CA. <sup>4</sup>Physics Dept, North Carolina State University, Raleigh, NC.

New quantitative techniques for chemical microanalysis which allow detailed study of protein polymer interactions are required for biomaterial interface optimization. We are particularly interested in identification of possible preferences of first sites of protein attachment to polymers used in blood contact medical applications where there may be competition for one type of segment over another. One model system which we are pursuing is a copolymer blend of polystyrene (PS) and polymethylmethacrylate (PMMA), which are immiscible in the bulk. A major question is whether or not the surface of such blends reflects the complete segregation known to be present in the bulk. If so, this would be a suitable model system to study preferential protein adsorption. We are exploring Scanning Transmission X-Ray Microscopy (STXM), a bulk sensitive technique, and Photoemission Electron Microscopy (PEEM), a more surface sensitive technique, to determine the surface and bulk morphology of as-cast and annealed PS-PMMA blends. These techniques use near edge X-ray absorption fine structure spectroscopy (NEXAFS) for chemical identification. Results from PEEM, STXM and atomic force microscopy (AFM) on several different PS-PMMA blends and on fibrinogen adsorbed on these polymer blend surfaces will be presented. X-ray microscopy is carried out at the Advanced Light Source (supported by DoE under contract DE-AC03-76SF00098), supported financially by NSERC (Canada).

#### 2:45 PM EE4.4

**Sr-TXRF ON Si-WAFER SURFACES: IMPROVED DETECTION LIMITS FOR TRANSITION METALS AND LOW Z ELEMENTS.** Katharina Baur, Sean Brennan and Piero Pianetta, Stanford Synchrotron Radiation Laboratory, Stanford University, Stanford, CA.

As the dimensions of integrated circuits continue to shrink also the amount of tolerable contamination on Si wafer surfaces decreases. Contaminants of primary concern are transition metals and light elements such as Al. Total Reflection X-ray Fluorescence (TXRF) spectroscopy using synchrotron radiation from the Stanford Synchrotron Radiation Laboratory (SSRL) is one of the most powerful techniques for trace impurity analysis on Si wafer surfaces. In addition, it is among the more sensitive techniques and the only one, which is non-destructive. In the first part we present the status of the transition metal work which has matured to a point where a facility exists at SSRL in which semiconductor companies are able to perform industrially relevant measurements at state of the art detection limits. This facility features clean wafer handling and automated data acquisition making routine analytical measurements possible. The best sensitivity demonstrated so far is  $3.4 \text{ E}7 \text{ atoms/cm}^2$  for a 5000 second count time corresponding to  $7.6 \text{ atoms/cm}^2$  for a standard 1000 second count time. This is more than a factor of 100 better than what can be achieved with conventional TXRF systems. The second part is focused on the detection of low Z elements such as Al. This is a challenging area due to a lower fluorescence yield as compared to transition metals and the presence of the much stronger Si fluorescence peak. For traditional energy-dispersive detection only the tunability of synchrotron radiation to excitation energies below the Si-K absorption edge leads to an acceptable detection limit for Al. However, this results in a substantial increase in background due to inelastic x-ray Raman scattering. This scattering dominates the background behavior of the Al-K fluorescence line, and consequently limits the achievable sensitivity for the detection of Al surface contaminants.

## SESSION EE5: SR METHODS APPLIED TO CEMENTITIOUS MATERIALS

Chairs: Angus P. Wilkinson and Stuart R. Stock  
Wednesday Afternoon, April 18, 2001  
Salon 14 (Marriott)

#### 3:30 PM EE5.1

**HIGH RESOLUTION TRANSMISSION SOFT X-RAY MICROSCOPY OF THE HYDRATION OF TRICALCIUM SILICATE.** Vincent Lamour, Paulo J.M. Monteiro, Dept of Civil and Environmental Engineering, University of California, Berkeley, CA; R. Livingston, Federal Highway Administration.

The hydration products of tricalcium silicate are extremely important for the development of strength and durability in portland cement concrete structures. These products are very sensitive to humidity; therefore traditional microscopy methods that require high vacuum are not appropriate for the determination of the morphology of the solids and kinetics of the reaction. To avoid such limitations our experimental work was done at the Center for X-ray Optics (CXRO) that built and operates a high-resolution soft x-ray microscope (XM-1) at the Advanced Light Source in Berkeley, California. The source, about 300 micron in size, is 17 m away from the sample and is demagnified by the condenser by a factor of 84 (at 2.4 nm wavelength, 517 eV). A condenser zone plate illuminates the sample and an objective zone plate forms an enlarged image on an x-ray CCD camera. While the optical path of the microscope is in vacuum, the sample is at atmospheric pressure, flushed by helium. The spatial resolution of the microscope is 43 nm. This research reports the changes in the morphology of the hydration products from early hydration (10 minutes) up to setting of the system. In particular, we focus our discussion on a product that appears to consist of bundles of dendrites that diverge as the growth process continues, resulting in the formation of a characteristic morphology which is narrowest in the middle and broadened at the end - the "sheaf-of-wheat" morphology. The formation of these products is discussed based on existing kinetics model.

#### 3:45 PM EE5.2

**TOMOGRAPHIC IMAGING OF MINERALOGY OF PORTLAND CEMENT CONCRETE DETERIORATION.** Richard Livingston, Wailarat Bumrongjaroen, Federal Highway Administration, Office of Infrastructure R&D, McLean VA; Roy Clarke, Univ. of Michigan, Dept. of Physics, Ann Arbor, MI; Ernest Williams, Oak Ridge National Laboratory, Oak Ridge, TN; Walter Lowe, Howard Univ. Dept. of Physics, Washington, DC.

The delayed formation of ettringite crystals is associated with Portland cement concrete deterioration. Determination of the ettringite content by X-ray powder diffraction is hindered by sampling problems caused by the presence of fine and coarse aggregates in the concrete. In situ measurement of the spatial distribution of ettringite content has been made using energy dispersive diffraction of synchrotron radiation. A 3-dimensional scan of a laboratory specimen of concrete was made at the MHATT-CAT station at the Advanced Photon Source. Using a CZT detector, 250 diffraction patterns were taken over a period of 6 hours.

#### 4:00 PM EE5.3

**MAPPING THE DISTRIBUTION OF CORROSION PRODUCTS IN CEMENT EXPOSED TO SULFATE USING ENERGY DISPERSIVE X-RAY DIFFRACTION.** Angus P. Wilkinson, Cora Lind, Georgia Institute of Technology, School of Chemistry and Biochemistry, Atlanta, GA; Stuart R. Stock, Georgia Institute of Technology, School of MS&E, Atlanta, GA; Kimberly E. Kurtis, and Nikhila Naik, Georgia Institute of Technology, School of Civil Engineering, Atlanta, GA; Dean R. Haefner, Peter L. Lee, SRI CAT, Advanced Photon Source, Argonne National Laboratory, IL.

Exposure of concrete structures to sulfate containing solutions and soil can lead to degradation and, in some cases, failure. The details of the processes occurring on sulfate exposure are not well understood. We are employing Energy Dispersive X-ray Diffraction (EDXRD) in combination with microtomography to examine both the chemical and microstructural changes that occur inside concrete specimens as they are subjected to sulfate attack. Bright beams of high energy X-rays from third generation synchrotron sources are capable of penetrating a considerable distance into typical cement specimens (~1 cm) and can be used to map the distribution of phases inside them on a length scale of ~ 100 microns. Either angle or energy dispersive measurements could in principle be used, but the energy dispersive experiment employs a fixed Bragg angle so that the volume sampled has a constant shape and size. Choosing the Bragg angle for such an experiment involves making a compromise. Low Bragg angles give a highly distorted sampling volume inside the specimen, but they allow the measurement of the large d-spacing reflections that are most characteristic of the phases in the specimen. Our initial EDXRD

studies were performed on beam line IID at the APS. The X-ray spectrum produced by this undulator is highly structured. We will present data showing the effects of varying both Bragg angle and undulator parameters on the EDXRD patterns obtained from cement paste samples. We will illustrate the potential of EDXRD as a technique for phase mapping using data obtained on test specimens. Use of the Advance Photon Source was supported by the U.S. Department of Energy under Contract No. W-31-109-Eng-38

#### 4:15 PM EE5.4

##### X-RAY SCATTERING STUDIES OF THE HYDRATION KINETICS IN TRICALCIUM AND DICALCIUM SILICATE PASTES.

Jay C. McLaughlin, Dan A. Neumann, NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD; Stephen FitzGerald, Oberlin College, Department of Physics, Oberlin; Silvina Pagola, Peter W. Stephens, SUNY Stony Brook, Department of Physics & Astronomy, Stony Brook, NY; Richard A. Livingston, Exploratory Research Team, Federal Highway Administration, McLean, VA.

Cement is the most widely used construction material, yet there is only a basic understanding of the hydration reaction that governs many of the final properties such as durability and strength. Tricalcium silicate is the most abundant phase in cement clinker, and thus represents the most simplified model for understanding the hydration reaction in cement. X-ray scattering using the facilities at the National Synchrotron Light Source (NSLS) has been used to monitor the hydration reaction in tricalcium silicate ( $C_3S$ ). The reaction is generally written:  $C_3S + (3-y-x)H \rightarrow C_xSH_y + (3-x)CH$ , where ( $C = Ca^0$ ,  $S = SiO_2$ , and  $H = H_2O$ ) where  $x$  determines both the number of moles of calcium hydroxide ( $CH$ ) formed and the  $C/S$  ratio of the  $C-S-H$  gel. By monitoring three regions of the spectra corresponding to the crystalline  $C_3S$ , crystalline  $CH$  and a region having peaks from both  $C_3S$  and  $CH$  we are able to monitor the progress of the reaction in real time. Three properties of the hydration reaction are being studied: temperature dependence, effect of particle size distribution, and the addition of varying amounts of  $C_2S$  to the reaction. Results from x-ray scattering are combined with data from Inelastic and Quasi-elastic neutron scattering to give a complete picture of their hydration reaction.

#### 4:30 PM EE5.5

ULTRA SMALL-ANGLE X-RAY SCATTERING CHARACTERIZATION OF SILICA FUME ADDITIVES FOR MICROSTRUCTURAL MODIFICATION OF CEMENT-BASED MATERIALS. Andrew Allen, Ceramics Division, NIST, Gaithersburg, MD; Richard A. Livingston, Office of Infrastructure R&D, Federal Highway Administration, McLean, VA.

Although silica fume addition to cement-based materials, to improve long-term strength development and durability, is of increasing interest, it is necessary to have a better understanding of the variability of the properties of the silica fume itself. Experiments using silica fume samples from five different sources found that significant differences in the evolution of the cement microstructure from one source to another. These effects can be related to the particle size distributions of the different fumes, measured using ultra-small-angle x-ray scattering (USAXS) using synchrotron radiation. The studies suggest that the presence in the fume of particles, which although fine are larger than a micrometer, is a more important issue in deciding fume performance than are the details of the ultrafine particle distribution.

#### 4:45 PM EE5.6

GRAZING INCIDENCE SMALL-ANGLE X-RAY SCATTERING APPLIED TO THE CHARACTERIZATION OF NANO-COMPOSITE THIN FILMS. David Babonneau, Amelia Suárez-García, José Gonzalo, Instituto de Optica, Madrid, SPAIN; Ivan R. Videnović, Michael G. Garnier, Peter Oelhafen, Institut für Physik der Universität Basel, Basel, SWITZERLAND; Michel Jaouen, André Naudon, Laboratoire de Métallurgie Physique, Université de Poitiers, Poitiers, FRANCE.

Nanocomposite thin films, consisting of metallic nanoparticles embedded in either a metallic or insulating matrix, play a crucial role in almost every field of technology and are of considerable interest for fundamental studies. The range of applications includes electronic devices and sensors, magnetic films, optical coatings, anti-corrosion and tribological coatings. For most applications, a precise control of the nanoparticle size and distribution within the host material is of crucial interest. Thus, original deposition methods as well as appropriate characterization techniques have been developed in recent years. In addition to transmission electron microscopy (TEM) and atomic force microscopy (AFM), which are direct imaging techniques, grazing incidence small-angle x-ray scattering (GISAXS) performed with synchrotron radiation is nowadays used as a powerful tool to study shape, size, and spatial correlation of embedded nanoparticles

as well as deposited islands. Indeed, TEM and AFM are limited to small sample areas while the GISAXS patterns represent a statistical average over a large number of nanoparticles ( $\approx 10^{12}$ ). Furthermore, GISAXS provides information on the in-depth nanoparticle dimensions, which is not accessible by AFM for embedded nanoparticles, or requires cross-section specimens as in the case of TEM.

The potential of the GISAXS technique will be illustrated by three examples. (i)  $Al_2O_3/Ag$  thin films suitable for ultrafast all-optical switching applications produced by pulsed laser deposition (two-dimensional growth). (ii)  $a-C:H/Au$  thin films as functional optical coatings elaborated by reactive magnetron sputtering (three-dimensional quasi-isotropic growth). (iii)  $BN/Fe$  thin films as magnetic recording media grown by ion-beam assisted deposition (three-dimensional columnar growth). It will be shown that GISAXS experiments, performed at the LURE synchrotron facility when using two-dimensional detectors, allow to get statistical information not only on the nanoparticle size and interparticle distance, but also on the size distribution both in the film plane and in the perpendicular direction.

#### SESSION EE6: POSTER SESSION

Chair: Patrick G. Allen

Wednesday Evening, April 18, 2001

8:00 PM

Salon 1-7 (Marriott)

#### EE6.1

STRUCTURE AND BONDING OF METALLIC NANOWIRES PREPARED IN NANOPOROUS ALUMINA MEMBRANES STUDIED BY EXAFS, XANES AND WAXS. Michael Kröll, Physics Department, Trinity College Dublin, IRELAND; Robert E. Benfield, John C. Dore, Didier Grandjean, Centre for Materials Research, School of Physical Sciences, University of Kent, Canterbury, UNITED KINGDOM; Günter Schmid, Institut für Anorganische Chemie, Universität GH Essen, GERMANY.

Nanoporous alumina membranes are prepared by anodizing aluminum foils in polyprotic acids. The pore diameter can be controlled by the anodizing voltage applied and ranges between 5 and 200 nm. Metal is deposited into the pores by an AC plating procedure. The nanowires produced in this way represent one-dimensional quantum wires with prospective application in electronic or magnetic devices. We have studied the structure and bonding of metallic nanowires including gold, silver, iron, cobalt and copper. EXAFS and XANES measurements were performed at the synchrotron radiation source at Daresbury, UK. WAXS measurements were made at ESRF Grenoble, France. Gold, silver and copper nanowires show the same structures and atom-atom distances as the corresponding bulk metals. Their EXAFS Debye-Waller factors, however, are slightly smaller than those of the bulk maybe indicating that the atoms are tighter held in the nanowire. XANES results show that the electronic structure of the nanowires is also similar to the bulk. EXAFS and XANES show a clear picture of build-up of metallic structure with nuclearity in a series of metal clusters, colloids and nanowires. Cobalt and iron nanowires are of interest because of their anisotropic ferromagnetic properties. Iron nanowires in pores of 12 and 24 nm diameter are structurally similar to bcc bulk iron, their XANES, however, show significant differences from the bulk. Cobalt nanowires within large pores show mere hcp structure with a preferred orientation of the hcp z-axis parallel to the long axis of the wires. If the pore diameter decreases a cobalt fcc phase which is known as a high temperature phase in the bulk becomes predominant. This structural change in small pores leads to a competition between magnetocrystalline anisotropy and the shape anisotropy of hcp cobalt as regards the magnetic properties.

#### EE6.2

STUDY OF  $TaSi_2$ -Si CRYSTALS WITH HIGH ENERGY SYNCHROTRON RADIATION AS TUNABLE WIDE-BANDPASS MONOCHROMATOR AND ANALYZER OPTICS. U. Rütt, Argonne National Laboratory, Materials Science Division, Argonne, IL; S.R. Stock, Georgia Institute of Technology, School of MS&E, Atlanta, GA; Z.U. Rek, Stanford Synchrotron Radiation Laboratory, Stanford, CA.

Single crystals of the in situ composite  $TaSi_2$ -Si are candidates for wide bandpass monochromators and analyzers for X-ray experiments. Two large crystals ( $32 \times 39 \times 7 \text{ mm}^3$  and  $32 \times 39 \times 30 \text{ mm}^3$ ) were studied in detail using 115 keV synchrotron radiation at the BESSRC beamline at the APS. For transmission geometry, the Si(111) reflection and 39 mm crystal thickness, rocking curve widths of 95 arcsec with reflectivities of 50% were measured over the entire crystal. Turning the crystal to an angle of  $45^\circ$  to the incident beam allowed a detailed study of the influence of the crystal thickness on the diffracted intensity by translating the crystal through the beam. For the observed range of sample thickness ranging from 5 mm to 12.5

mm, the FWHM of the rocking curve increased linearly from 29 arcsec to 53 arcsec. The greatest gain in integrated intensity was obtained for 8-9 mm thickness where FWHM= 40 arcsec. If this crystal is used as monochromator, it would provide 40 times more intensity than a perfect silicon crystal with an energy bandwidth of 1 keV at 115 keV synchrotron radiation. With the broadening of the rocking curve width a plateau across the peak maximum is developed. Its width increased from 5 to 25 arcsec with increasing crystal thickness from 5 to 12.5 mm. This plateau allows these crystals to be used as analyzer crystals in diffraction experiments, i.e. as very narrow slits to suppress background. A plateau width of about 5-20 arcsec for the analyzer crystal is needed to ensure, that the whole intensity scattered from the sample is diffracted by the analyzer crystal. The simple expedient of changing the crystal thickness alters the plateau width of the analyzer crystal and tunes its acceptance to the needs of the sample under study.

### EE6.3

SYNCHROTRON X-RAY REFLECTIVITY ANALYSIS OF (CdS/POLYMER) MULTILAYERS. J. Koo, B.H. Seung, K.-B. Lee, POSTECH, Dept of Physics and Electron Spin Science Ctr, Pohang, KOREA; Y.J. Park, Pohang Accelerator Laboratory, Pohang, KOREA; J. Cho, S.-H. Lee, H. Kang, K. Char, Seoul National Univ, School of Chemical Engineering, Seoul, KOREA.

X-ray reflectivity analysis using synchrotron radiation has been carried out on organic/inorganic multilayer films. The films composed of cationic poly(allylamine hydrochloride)(PAH) and anionic poly(sodium 4-styrenesulfonate)(PSS) and inorganic cadmium sulfide(CdS) nanoparticles with surrounding negative charges, were grown using spin self-assembly method. In these cases, multilayer Bragg peaks as well as Kiessig fringes were clearly shown, indicating distinct interfaces between CdS and organic layers. Results of the analysis on structural parameters, such as density profiles and interface roughnesses, for the multilayers will be presented.

### EE6.4

X-RAY REFLECTIVITY AND GISAXS STUDY OF DE-RELAXATION IN Kr IMPLANTED Si. P. Dubcek, Synchrotron ELETTRA, Bassovizza, ITALY; B. Pivac, R. Boskovic Inst., Zagreb, CROATIA; O. Milat, Inst. for Physics, Zagreb, CROATIA; S. Bernsdorff, Synchrotron ELETTRA, Bassovizza, ITALY.

The structural changes induced in single crystal silicon implanted with Krypton above the amorphisation threshold were studied by X-ray reflectivity together with Grazing Incidence Small Angle X-ray Scattering technique. Silicon samples were implanted with Krypton with two different ion energies. A well-defined layer, 220 nm thick of amorphous silicon, rich in Krypton, was formed below the top, undisturbed layer, but only after sample annealing. A series of samples consist of as-implanted sample, a sample relaxed by thermal annealing at 720 K and a number of samples with increased level of defects induced by additional Kr implantation. Additional implantation caused changes in the films composition and thickness, which was well evidenced in reflectivity curve, while only minor changes of surface roughness and critical angle were detected in GISAXS spectra.

### EE6.5

ELASTIC PROPERTIES OF MIXED CATIONIC-ANIONIC SURFACTANT BILAYERS: HIGH RESOLUTION SAXS CONFIRMS LOW BENDING MODULUS. B.A. Coldren, H.E. Warriner, J.A. Zasadzinski, Department of Chemical Engineering and Materials Research Laboratory, Univ of California-Santa Barbara, CA.

A key to enlarging the realm of surfactant applications has been the 'physical synthesis' of new materials by mixing surfactants to achieve a desired set of properties. Mixed surfactants produce new microstructures by altering the intermolecular and interaggregate forces in ways impossible for single surfactants. This has been clearly demonstrated in the mixed cationic-anionic (catanionic) vesicle systems. While there have been various theoretical predictions of the physical properties of catanionic surfactant membranes, surprisingly few direct experiments have been conducted in order to quantify characteristics such as elasticity, permeability, spontaneous curvature, stability, and interactions that ultimately govern surfactant microstructure. Our recent work has included directly measuring the elastic properties of catanionic bilayers via analysis of the equilibrium vesicle size distribution using cryogenic transmission electron microscopy. Most of the catanionic systems investigated possessed a relatively low bending elasticity,  $K$ , of order  $kT$ . Our current studies conducted at the Brookhaven NSLS focus on independently verifying these measurements, as well as gaining further insights into the nature of intermembrane interactions, by instead looking at the bulk lamellar phases of similar composition. Via line-shape analysis of high resolution synchrotron scattering data, we perform measurements of the membrane bending modulus as a function of surfactant structure, cationic-anionic ratio, and polymer inclusions. Results indicate that,

indeed, most cationic-anionic bilayer systems display a characteristically low bending modulus over a broad range of composition.

### EE6.6

A PROGRAM USED IN THE ANALYSIS OF STRESS GRADIENTS BELOW THE VERY SURFACE BASED ON THE MULTI-ENERGY METHOD. Yanan Xiao, Myungae Lee, Dale E. Wittmer, Southern Illinois Univ, Dept of Mechanical Engineering and Energy Processes; Susan M. Mini, Northern Illinois Univ, Dept of Physics, DeKalb, IL; Tim Graber, James P. Viccaro, The Center for Advanced Radiation Sources, The University of Chicago, Argonne, IL.

The residual stress gradient distribution below the very surface of a material is an important factor for engineering materials. With the availability of an energy-tunable intense synchrotron radiation source, it becomes easier to analyze the stress gradient below the very surface, based on the multi-energy X-ray diffraction method. In order to evaluate the sample from a known stress gradient distribution or to calculate the stress gradient distribution below the very surface, according to the experimental results, a program was developed. Another program for calculating the X-ray absorption coefficients of all of the elements was embedded in this program. This means that all of the compounds could be analyzed by this program. As an example, in the present study, the relation between X-ray energy and residual stress as well as the relation between X-ray energy and the residual stress gradient are discussed according to the calculated result for a selected silicon nitride composition.

### SESSION EE7: MAGNETIC MATERIALS

Chairs: Susan M. Mini and Patrick G. Allen  
Thursday Morning, April 19, 2001  
Salon 14 (Marriott)

### 8:45 AM \*EE7.1

CORRELATED LOCAL ATOMIC DISPLACEMENTS: THE MICROSCOPIC ORIGINS FOR MACROSCOPIC PHENOMENA. Frank Bridges, Physics Dept. University of Calif. Santa Cruz, CA.

In many systems for which there are several atoms in the unit cell, the displacements of the atoms may be locally correlated even though there is no long range coherence. Such displacements can play an important role in determining various macroscopic properties. We consider several examples to demonstrate this phenomena - the local distortions in the colossal magnetoresistive (CMR) and charge-ordered manganites, magnetic field induced distortions in CMR materials that are connected to macroscopic magnetostriction and correlated displacements of tetrahedral units within the negative thermal expansion material  $ZrW_2O_8$ . The distortions in the CMR materials observed using XAFS change rapidly just below  $T_c$  and are attributed to the formation of polarons as the temperature is increased through  $T_c$ . In the ferromagnetic state, the lattice is more ordered for CMR systems; consequently applying a magnetic field should decrease the distortion. Such an effect has been observed and is locally a much larger effect than the macroscopic magnetostriction observed. Finally, in  $ZrW_2O_8$  the tetrahedral and octahedral units are very rigid and even the atom-pair distances for W-Zr have a small pair distribution function (PDF) width. However, for the W-W pair, the PDF width grows rapidly with T, indicating correlated movements of the entire WO tetrahedral unit.

### 9:15 AM EE7.2

A CORRELATION OF Mn-K XAS NEAR EDGE STUDIES OF MANGANATE-PEROVSKITE BASED MATERIALS. M. Croft, Physics Dept., Rutgers Univ., Piscataway, NJ; G. Popov, G. Veith, Chemistry Dept., Rutgers Univ., Piscataway, NJ; P. Ansari, Physics Dept., Seton Hall Univ., So. Orange, NJ; T. Tyson, Physics Dept., New Jersey Institute of Technology, Newark, NJ; M. Greenblatt, Chemistry Dept., Rutgers Univ., Piscataway, NJ; S-W. Cheong, D. Sills, Physics Dept., Rutgers Univ., Piscataway, NJ.

Driven by technological interest in colossal magnetoresistance, there has been a wealth of new perovskite-manganite based materials synthesized in recent years. The interplay between competing Jahn Teller (JT), charge-orbital (CO) ordering and ferromagnetic (FM) double exchange interactions dominate the physics of these materials. A sophisticated repertoire of chemical substitution techniques has been developed to systematically tune the balance between these competing interactions for desired physical properties. Since the  $Mn^{3+}/Mn^{4+}$  ratio is crucial to most of these interactions, Mn-K edge x-ray absorption spectroscopy (XAS) has been extensively exploited to probe this important valence ratio. The sheer scope of the systems studied, now allows some systematic observations on the competing roles of the FM, JT and CO interactions in determining the Mn-K near edge structure. In this paper, the common threads of XAS-near

edge behavior in a diverse series of materials will be discussed. Specifically the systems to be compared are: the prototype doped  $R_{1-x}A_xMnO_3$  ( $R=La, Bi, \& Ce$ ) and ( $A=Ca, Ba, Sr, \& Pb$ ) materials, where a wide range of competing interactions is traversed: the  $RMnO_3$  ( $R=La, Pr, \& Nd$ ) compounds, where a varying JT interaction strength occurs; and the Rudleson-Popper, layered  $[ATO_3]_n-[AO]$  compounds with  $T=(Mn, Fe)$  ( $A=Ca \& Sr$ ) and  $n=2, 3, \infty$ , where the substitution induces mutual localization of the T-site d-orbitals. Special attention will be paid to the discussion of the pre-edge features in these materials. In particular the majority-spin  $e_g$  state feature and its variation with varying JT and FM interactions will be focused upon. The reflection of local distortions and varying valence in the main edge will also be discussed.

#### 9:30 AM \*EE7.3

FLUCTUATIONS AND PHASE SEPARATION: DRIVING MECHANISMS FOR ORDERING IN PEROVSKITE MANGANITES. Christie S. Nelson, Brookhaven National Laboratory, Department of Physics, Upton, NY.

X-ray scattering techniques are used to study the driving mechanisms for ordering in two perovskite manganites:  $La_{0.7}Ca_{0.3}MnO_3$  and  $Pr_{0.7}Ca_{0.3}MnO_3$ . Due to variation in the strength of the electron-phonon coupling resulting from the different sizes of the trivalent cations, these two samples exhibit completely different low temperature phases—ferromagnetic metallic and antiferromagnetic insulating, respectively. However, in the high temperature-paramagnetic-insulating phases, the behaviors of the two samples are found to be quite similar. Specifically, both exhibit isotropic fluctuations with a  $(0.5\ 0\ 0)/(0\ 0.5\ 0)$  ordering wavevector and a correlation length of 1–2 lattice constants. The fluctuations can be interpreted in terms of correlated polarons, with a structure consistent with a CE-type orbital order domain. Differences in behavior arise between the two samples only as they are cooled through their respective transition temperatures. While  $La_{0.7}Ca_{0.3}MnO_3$  becomes ferromagnetic metallic,  $Pr_{0.7}Ca_{0.3}MnO_3$  exhibits three low temperature phases. The latter sample thus provides an illustration of the importance of phase separation in the manganites, and we have used resonant x-ray scattering techniques—measuring the polarization and azimuthal dependences of the scattering—to investigate the nature of the three phases.

Work done in collaboration with M. v. Zimmermann, J.P. Hill, Doon Gibbs, V. Kiryukhin, S-W. Cheong, D. Casa, B. Keimer, Y. Tokura, T. Gog, and C.T. Venkataraman.

The work at Brookhaven, both in the Physics Department and at the NSLS, was supported by the U.S. DOE, Division of Materials Science, under Contract No. DE-AC02-98CH10886.

Work at the CMC beamlines is supported, in part, by the Office of Basic Energy Sciences of the U.S. DOE and by the NSF, Division of Materials Research. Use of the APS was supported by the Office of Basic Energy Sciences of the U.S. DOE under Contract No. W-31-109-Eng-38.

#### 10:30 AM EE7.4

A SOFT X-RAY UNDULATOR BEAMLINE WITH CIRCULAR AND VARIABLE LINEAR POLARIZATION FOR HIGH RESOLUTION SPECTROSCOPY OF MAGNETIC MATERIALS. Anthony T. Young, Elke Arenholz, Jun Feng, Howard Padmore, Steve Marks, Ross Schlueter, Egon Hoyer and Christoph Steier, Advanced Light Source, Lawrence Berkeley Laboratory, Berkeley, CA.

The use of polarized x-rays to study the chemical and physical properties of materials has become an experimental technique of great utility. In particular, linearly and circularly polarized radiation has been used to study the magnetic properties of ferro- and antiferromagnetic materials. The Advanced Light Source at Lawrence Berkeley Laboratory has completed a new beamline, Beamline 4.0.2, which has been optimized for performing high resolution spectroscopy using circularly and linearly polarized x-rays. This new beamline has, as its photon source, an elliptically polarizing undulator (EPU). This insertion device directly produces high flux, high brightness beams of x-rays of variable polarization, from linear horizontal to circular to linear vertical. The output from the EPU is directed to a monochromator which produces high resolution beams from 90 eV to beyond 1600 eV. This paper will present the operating characteristics and key performance parameters of the new beamline. Recent experimental results illustrating the utility of circularly and linearly polarized x-rays to studies of advanced materials will also be presented.

This work has been supported by the Director, Office of Science, Offices of Basic Energy Sciences and Biological and Environmental Research, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

#### 10:45 AM EE7.5

MAGNETISM OF SMALL, DEPOSITED IRON CLUSTERS. J. Tobias Lau, A. Föhlisch, W. Wurth, II, Institut für

Experimentalphysik, Universität Hamburg, Luruper, Hamburg, GERMANY.

Understanding the magnetic properties of nanostructured materials is of great importance to promote their technological application in high-density magneto-optical recording devices. Circularly polarized synchrotron radiation is a powerful tool to investigate these properties by element specific X-ray magnetic circular dichroism (XMCD) studies. In a recent experiment we have been able to show that even highly diluted samples such as size selected transition metal clusters deposited onto a substrate can be investigated by XMCD at third generation synchrotron radiation facilities (BESSY II, Berlin). Size selected  $Fe_n$  clusters ( $n=1-13$ ) were deposited onto ultrathin Ni films ( $\approx 20$  monolayers) grown on a Cu(100) substrate. To obtain well defined cluster samples, no more than 0.03 monolayers of  $Fe_n$  were deposited under soft landing conditions. Sample preparation was carried out in UHV. Because of their perpendicular magnetic anisotropy, ultrathin Ni films can be magnetized remanently perpendicular to the sample surface, providing a magnetic field to align the magnetic moments of the  $Fe_n$  clusters.

We obtain strong dichroic absorption signals from the clusters at the Fe  $L_{2,3}$ -edges. All  $Fe_n$  clusters are coupled ferromagnetically to the Ni substrate. With the use of sum rules, ratios of spin to orbital magnetic moments were determined as a function of cluster size. The clusters show variations in their ratio of orbital to spin magnetic moment, with the highest ratio of  $m_{orb}/m_{spin}$  observed for  $Fe_8$ .

#### 11:00 AM \*EE7.6

$Fe_3O_4$ : EVIDENCE FOR HALF-METALLIC-FERROMAGNETIC BEHAVIOR FROM SPIN POLARIZED PHOTOEMISSION.

J.G. Tobin, Lawrence Livermore National Laboratory, Livermore, CA; S.A. Morton, G.D. Waddill, University of Missouri-Rolla, Rolla, MO; S.A. Chambers, Pacific Northwest National Laboratory, Richland, WA; S. Kim and I. Schuller, University of California-San Diego, La Jolla, CA.

Many materials have been predicted to be half metallic ferromagnets, yet despite extensive study, remarkably little truly compelling evidence for half metallic behavior has emerged. One technique that can potentially yield a definitive answer to the question of half metallic character is spin polarized photoemission and it is from this technique that the strongest evidence to date has emerged [1]. Using the spin-resolving photoelectron spectrometer at the Spectromicroscopy Facility (Beamline 7) at the Advanced Light Source [2], we have found evidence for half-metallic behavior in thin films of magnetite. Thin films of magnetite hold out the possibility of use in devices as pure spin sources. Because our spin resolving experiments are performed at higher photon energies, we were able to monitor the spin polarization of the near Fermi energy electrons without resorting to destructive surface cleaning techniques, using the samples 'as is'. Furthermore, we have demonstrated that harsh sample cleaning procedures such as ion etching causes the loss of the desired spin polarization, which may help explain the failure of other previous experiments to observe half metallic behavior. The ability to perform the experiments at higher energies is a direct result of the high brightness of the ALS and is probably a unique capability of 3rd Generation Synchrotron Radiation Sources. The experiments at the ALS are founded upon growth and characterization studies at UCSD and PNNL. Magnetite films were prepared at UCSD by reactive sputtering. Epitaxial magnetite films were grown on MgO and sapphire substrates with precise control of gas flows and substrate temperature. Their structure was characterized by RHEED, LEED, and XRD. PNNL samples were grown under MBE conditions and transferred to the ALS via a vacuum suitcase system. By measuring the polarization as a function of emission angle and photon energy, and combining these measurements with a substrate overlayer model, we have gained substantial insight into the nature of magnetite. Furthermore, our spin resolved spectra demonstrate close agreement with simulated spectra derived from theoretical one electron density of states calculations [3]. Further experiments are in progress.

[1] Park et al, Nature 392, 794 (1998); Phys. Rev. Lett. 81, 1953 (1998).

[2] J.G. Tobin et al, MRS Symp. Proc. 524, 185 (1998).

[3] Z. Zhang and S. Satpathy, Phys. Rev. B. 44, 13319 (1991).

#### 11:30 AM EE7.7

X-RAY MAGNETOOPTICS IN LANTHANIDE MATERIALS.

K. Starke, F. Heigl, A. Vollmer and G. Kaindl, Institut für Experimentalphysik, Freie Universität Berlin, Berlin-Dahlem, GERMANY.

Magneto-optical methods in the visible light regime generally lack element-specificity, which has become a considerable shortcoming in research on advanced heteromagnetic systems. Using circularly polarized soft x rays tuned to a 4d-4f core-level transition of a lanthanide element, the specularly reflected x-ray intensity changes proportionally to the magnetization of this element and, e.g.

hysteresis  $M(H)$  as well as temperature dependent magnetization  $M(T)$  are easily measured element-specifically. In contrast to using visible light, temperature dependent 4d-4f magneto-optical signals are not influenced by the thermal lattice expansion.

This work is supported by the BMBF (05 SC6 KEB-8) and the DFG (Sfb 290, TP A6).

#### SESSION EE8: X-RAY ABSORPTION AND PHOTOEMISSION

Chair: Tony W.H. Van Buuren

Thursday Afternoon, April 19, 2001

Salon 14 (Marriott)

##### 1:30 PM EE8.1

**ELECTRONIC STRUCTURE OF Ge-NANOCUSTER FILMS PROBED WITH SYNCHROTRON RADIATION.** C. Bostedt, University of Hamburg, GERMANY and Lawrence Livermore National Lab, Livermore, CA; Tony van Buuren, N. Franco, L.J. Terminello, Lawrence Livermore National Lab, Livermore, CA; T. Müller, HASYLAB at DESY, GERMANY.

Clusters and nanocrystals show a wide variety of novel electronic, magnetic and catalytic properties. Germanium clusters are of particular interest since, as recent publications suggest, they display a strong blue luminescence. However, it is not clear, if this luminescence is due to surface species, oxide layers or quantum confinement. X-ray absorption spectroscopy (XAS) and Photoemission (PES) were measured on thin films of Germanium (Ge) clusters. The clusters were synthesized *in situ* by thermal vaporization of Ge in a He buffer gas and subsequently deposited. The average diameter of the clusters could be varied between 1nm and 5nm. Characterization of the nanoclusters in size and shape was done by non-contact atomic force microscopy. X-ray absorption spectroscopy at the Ge L-edge was used to measure the shift of the conduction band of the Ge-clusters as a function of particle size. We find, that the conduction band of the clusters is blueshifted compared to bulk-Ge, in agreement with quantum confinement theory. The blueshift ranges from 0.2eV to 0.4eV for clusters between 4nm and 2nm. Photoemission data shows a very small shift of around 0.1eV of the valence band in clusters of around 3nm in size. Measurements of the Ge3d plasmons show a strong increase of the surface plasmon compared to the bulk plasmon in clusters. Comparison of this work to previous work done on Si-clusters of the same size and prepared in the same manner show, that the conduction band shift in Ge-clusters is much larger for clusters of the same size. Effective mass calculations of Si and Ge clusters confirm this effect. C. Bostedt acknowledges a fellowship from the German Academic Exchange Service DAAD in the HSP-III program, N. Franco from the Spanish Education and Culture Office. The work is supported by the US-DOE, BES Material Sciences under contract W-7405-ENG-48, LLNL.

##### 1:45 PM EE8.2

**IMAGES OF LATERAL BAND-BENDING ACROSS Si PN JUNCTION SURFACES USING SCANNED XRAY PHOTOEMISSION ELECTRON MICROSCOPY.** R.J. Phaneuf, M. Marsi, L. Gregoratti, S. Günther and M. Kiskinova, Department of Materials and Nuclear Engineering, University of Maryland, College Park, MD and Sincrotrone Trieste, Trieste, ITALY.

In this talk I'll discuss the results of characterizations of lateral Si pn-junction arrays using spectroscopically-resolved scanning soft-x-ray photoemission microscopy (SPEM), a technique made practical by the advent of ultrabright third generation synchrotron light sources, such as Elettra, in Trieste, Italy. The presence of electrically active surface states at an oxide/silicon interface leads to a 'bending' of the electron energy levels in the near-surface region, an effect which can be exploited in imaging devices on which this bending is nonuniform. This variation can be probed directly by measuring the spatial dependence of the kinetic energy of electrons emitted from the characteristic Si core energy levels. Intensity maps acquired at a series of closely spaced energies spanning the Si 2p core level allow for the creation of an 'image' of the variation of the near surface band bending across the depletion region of a pn junction. These spectroscopically and spatially resolved (resolution of approximately 70 nm) images also allow characterization of anomalies in the dopant profile across lithographically fabricated devices. I'll also discuss variations in the band bending (or 'lineup') across the devices with oxide preparation, and the effect of surface photovoltage. Work supported by the Laboratory for Physical Sciences, an NSF-MRSEC and Synchrotron Trieste.

##### 2:00 PM EE8.3

**IN SITU X-RAY ABSORPTION SPECTROSCOPY IN THE SOFT X-RAY RANGE: NOVEL PROSPECTS FOR THE CHEMICAL CHARACTERIZATION OF SOLID STATE SURFACES AT HIGH**

**PRESSURE AND HIGH TEMPERATURE.** Th. Schedel-Niedrig, Hahn-Meitner-Institut, GERMANY; M. Hävecker, A. Knop-Gericke, R. Schlögl, Fritz-Haber-Institut, GERMANY; and P. Reinke, Universität Basel, SWITZERLAND

An instrumentation equipped with total electron yield detectors was designed and constructed for *in situ* X-ray absorption spectroscopy (XAS) investigations in the soft X-ray range ( $100 \text{ eV} \leq h\nu \leq 1000 \text{ eV}$ ) at elevated pressures (mbar range) and sample temperatures ( $T \leq 1000 \text{ K}$ ) [1]. This allows, for the first time, XAS studies in a surface-sensitive mode of the light elements ( $Z = 3-15$ ). Furthermore, the gas phase XAS and the surface-related XAS of the solid state phase can be collected simultaneously in order to correlate the gas/solid reaction rate with the surface electronic structure under working conditions in a flow-through mode.

The novel experimental tool presents a contribution to the experimental overcoming of the "pressure gap" in material science. In this work examples are presented belonging to the field of heterogeneous catalysis [2] and to the reactivity of diamond surfaces [3]. Additionally, prospects for studies in the field of solar cells will be given.

[1] Th. Schedel-Niedrig *et al.*, Nucl. Instr. Meth. A, **406** (1998) 311; Deutsches Patent Nr. 198 10 539.

[2] Th. Schedel-Niedrig *et al.*, Appl. Surf. Sci. **142** (1999) 438; Phys. Chem. Chem. Phys. **2** (2000) 3473; M. Hävecker *et al.*, Agnew. Chem. Int. Ed **37** (1998) 1939.

[3] P. Reinke *et al.*, Surf. Sci. **447** (2000) 229.

##### 2:15 PM EE8.4

**EXAFS AND XANES ANALYSIS OF BALL-MILLED IRON-NICKEL ALLOYS.** P.J. Schilling, Univ of New Orleans, Dept of Mechanical Engineering, New Orleans, LA; V. Palshin and R.C. Tittsworth, Louisiana State Univ, Center for Advanced Microstructures and Devices, Baton Rouge, LA; E. Ma and J.-H. He, Johns Hopkins University, Dept of MS&E, Baltimore, MD.

EXAFS and XANES analysis have been applied in a study of nano-crystalline iron-nickel alloys prepared by high-energy ball-milling. Samples were prepared with overall compositions spanning the two-phase region. Using XANES analysis, the phase fractions and compositions of the two coexisting solid solutions were determined to characterize the ball-milled two-phase region in this negative heat-of-mixing system, and compare it to the positive heat-of-mixing Fe-Cu system.

##### 2:30 PM EE8.5

**PHOTOEMISSION AND PHOTOABSORPTION STUDY OF  $\text{YNi}_{2-x}\text{Co}_x\text{B}_2\text{C}$  SUPERCONDUCTORS.** L.-S. Hsu, C.-J. Chen, Dept of Physics, National Chang-Hua University of Education, Chang-Hua, TAIWAN, G.Y. Guo, Dept of Physics, National Taiwan University, Taipei, TAIWAN; M.-D. Lan, Dept of Physics, National Chung Hsing University, Tai-Chung, TAIWAN; J.-F. Lee, Synchrotron Radiation Research Center, Hsinchu, TAIWAN.

The electronic structures of five polycrystalline  $\text{YNi}_{2-x}\text{Co}_x\text{B}_2\text{C}$  ( $x=0, 0.05, 0.1, 0.15, \text{ and } 0.2$ ) borocarbide superconductors were studied by photoemission and photoabsorption spectroscopy around the Ni (Co) 3p and 2p absorption thresholds, and Ni (Co) K edges. The Ni (Co) 2p core-level spectra yield the asymmetry index, which correlates with the density of states (DOS) at the Fermi level ( $E_F$ ) for samples with different concentration of Co dopant. The valence-band (VB) spectra are compared with the DOS curves obtained from band-structure calculation. The VB satellite is resonantly enhanced around the Ni 3p threshold. The constant-initial-state spectra show typical Fano-type lineshape. The number of 3d holes per Ni atom is estimated theoretically to be 0.84 for the  $x=0$  compound; and 0.89 and the 0.95 for the  $x=0.1$  and 0.2 compounds, respectively. The Ni K-edge x-ray absorption near-edge spectra are compared with those derived from theory. The bonding characters between the Ni and Co atoms are determined from the Ni (Co) K-edge extended x-ray absorption fine-structure spectra. The decrease of the superconducting transition temperature with addition of Co atoms in these intermetallics is due to a decrease of the DOS at  $E_F$ .

#### SESSION EE9: X-RAY SCATTERING AND INTERFACES

Chairs: Susan M. Mini and Pedro A. Montano

Friday Morning, April 20, 2001

Salon 14 (Marriott)

##### 8:30 AM EE9.1

**INTERDIFFUSION STUDIES IN  $\text{Si/Si}_{1-x}\text{Ge}_x$  HETERO-STRUCTURES.** Marc A. Mander, Daniel B. Aubertine, Ann F. Marshall, and Paul C. McIntyre, Stanford Univ., Department of MS&E, Stanford, CA; Glen Wilk, Lucent Bell Laboratories, Murray

Hill, NJ; Pat Mooney and Jack Chu, IBM T.J. Watson Research Center, Yorktown Heights, NY.

Several studies of epitaxial Si/SiGe heterostructures have observed evidence of a rapid, non-linear interdiffusion during post-deposition anneals. This initially rapid interdiffusion is currently attributed to the relaxation of misfit stresses during annealing. Understanding coupled interdiffusion and stress relaxation is important to device engineers seeking to exploit the novel electrical and optical properties of strained multilayers. We employ synchrotron radiation in symmetric x-ray scattering experiments to obtain quantitative information about the strain-relaxation mechanisms in post-deposition annealed multilayers (10 bilayers of 5nm Si/5nm Si<sub>0.88</sub>Ge<sub>0.12</sub> grown on a Si(001) substrate by MBE or CVD). A high resolution 2-circle goniometer is used to obtain precise information about the evolution of the multilayer structure as a function of annealing time. For example, multilayer peak shifts in high-angle symmetric and asymmetric XRD scans reveal strain relaxation in the multilayer. In addition, attenuation of the multilayer satellite peaks after post-deposition annealing and advanced data scaling analysis can be used to extract both the interdiffusion coefficient  $D_I$  and the activation energy for the multilayer interdiffusion. Low-angle peaks due to the chemical modulation provide additional, unambiguous insight into the evolution of the multilayer structure.

#### 8:45 AM EE9.2

INELASTIC X-RAY SCATTERING FROM 6H-SiC. P.A. Montano, Materials Science Division, Argonne National Laboratory and Dept. of Physics, University of Illinois at Chicago, IL; D.L. Price, Dept. of Physics, University of Memphis, TN; A.T. Macrander, Advanced Photon Source, Argonne National Laboratory, IL; B.R. Cooper, Dept. of Physics, West Virginia Univ., WV.

Inelastic x-ray scattering were performed at momentum transfers,  $q$ , ranging from  $0.47 \approx -1$  to  $2.63 \approx -1$  along the  $c$ -axis, i.e., along  $[00 \cdot 1]$ . These were compared to spectra obtained for  $q$  along the  $[100]$  direction. Comparison of the two sets of data reveals an orientation dependence of the spectra, except for a single peak at 23 eV that occurs for both directions at low  $q$ . This peak is identified as a bulk plasmon excitation. We performed theoretical calculations of the dynamical structure factor, using a full-potential LMTO method. The results were compared with the experimental measurements, a good agreement was found between the measured  $S(q,w)$  and the calculated one. The orientation dependence of the other spectral features demonstrates that the band structure plays a significant role in their origin. A modification to  $e^{-1}(q,w)$  was also investigated, it consisted of including a "local field factor". The effect of this correction, within the range of  $q$  in our measurements, is to broadly raise and lower energy portions of  $S(q,w)$ , in such a way as to not affect the detailed structure of the calculated results. We also explored the effect of including the off-diagonal elements on the structure factor. Inclusion of the off-diagonal terms had a substantial effect upon the detailed nature of the structure factor.

#### 9:00 AM EE9.3

X-RAY SCATTERING MEASUREMENTS OF THE Ag(111) SURFACE THERMAL EXPANSION. Cristian E. Botez, William C. Elliott, Paul F. Miceli, University of Missouri-Columbia, Department of Physics and Astronomy, Columbia, MO; Peter W. Stephens, State University of New York, Department of Physics, Stony Brook, NY.

The observation of an anomalously large thermal expansion of Ag(111) by medium-energy ion-scattering (MEIS) [P. Satiris *et al.*, Phys. Rev. Lett. **72**, 3572 (1994)] has led to extensive theoretical investigations of this surface. Surprisingly, there is a persisting disagreement between the results from different theoretical methods: while molecular dynamics (MD) simulations indicate that the surface expands almost bulk-like at all temperatures, quasi-harmonic approximation (QHA) calculations predict a large high-temperature surface thermal expansion. Motivated by this controversy, we reinvestigated the thermal expansion of Ag(111) within the temperature interval between 300 and 1100K (90% of the bulk melting point), using synchrotron x-ray diffraction, a technique that is well known for its ability to accurately determine the surface and the bulk lattice spacings simultaneously. Our specular reflectivity data show no evidence of a large surface thermal expansion. At all temperatures we find that the first and the second interlayer separations at the surface,  $d_{12}$  and  $d_{23}$ , differ from their bulk counterpart,  $d$ , by less than 1%, indicating that the surface is virtually unrelaxed relative to the underlying bulk crystal. This behavior is in good agreement with results from MD simulations, whose predictions for the surface vibrational amplitudes are also consistent with our experimental determinations.

Support is acknowledged from NSF under contracts (PWS) DMR-9202528 and (PFM, CEB, WCE) DMR-9623827 and MISCON under DOE grant DE-FG02-90ER45427. The SUNY X3 beam line is supported by the DOE, under contract DE-FG02-86ER45231 and the

NSLS is supported by the DOE, Division of Material Sciences and Division of Chemical Sciences.

#### 9:15 AM EE9.4

ANOMALOUS X-RAY SCATTERING FROM MOLYBDENUM-GERMANIUM ALLOYS. Hope Ishii, Sean Brennan, Arthur Bienenstock, Stanford University, Stanford Synchrotron Radiation Laboratory, Stanford, CA.

The technique of anomalous x-ray scattering (AXS) requires energy tunability, commonly from a synchrotron source, to change the atomic scattering factor by varying the incident x-ray energy near the atomic absorption edges of the elements in a sample. The resulting changes in diffracted intensities can be extracted as chemically-specific structural information in the form of differential and partial distribution functions (DDFs and PDFs). However, the solution to the extraction problem is "ill-conditioned," and small errors in measurements of elastically-scattered intensity result in large errors in the distribution functions. In a typical AXS experiment, the energy detection window of a solid state detector accepts not only the elastic scattering but also the inelastic scattering which must be subtracted from the total intensity using calculated values. An improvement to this scheme is to experimentally eliminate the inelastic scattering. We show that by combining a variable-focus, dispersive analyzer crystal with a position-sensitive linear detector<sup>1</sup>, we obtain low background and sufficient energy resolution to discriminate against the inelastic  $K_{\beta}$  resonant Raman and Compton scattering over most of the reciprocal space range probed. Experimentally-determined anomalous scattering factors also improve the accuracy of the resulting distribution functions. The sputtered Mo-Ge amorphous alloy system demonstrates a metal-insulator transition in the Ge-rich composition range where phase separation also occurs. It has been suggested that the M-I transition in many of these intermetallic systems is due to percolation of the conducting metal-rich phase. We apply AXS with experimental removal of inelastic scattering to  $\alpha$ -MoGe<sub>3</sub>, the metal-rich endpoint for phase separation in the sputtered Mo-Ge amorphous alloy system. The metastability of this composition is of particular interest because the stable phase in the equilibrium system is MoGe<sub>2</sub>.

<sup>1</sup>G.E. Ice and C.J. Sparks, *Nuc. Instr. Meth.*, **A291**, 110-116 (1990).

#### 9:30 AM EE9.5

X-RAY STANDING WAVES WITH UNDULATOR BEAMS: PROBING IMPERFECT CRYSTALS. A. Kazimirov, M.J. Bedzyk, D.L. Marasco, S.K. Streiffer, Northwestern University, Argonne National Lab.

The standard X-ray standing wave technique based on the interference of the incident and the Bragg-diffracted X-ray beams requires high crystalline quality single crystals as standing wave generators. Only a few crystals (such as Si, Ge, GaAs) are sufficiently perfect to satisfy this strict criterion of dynamical diffraction. We demonstrate that by using the unique brightness of the undulator SR source the scope of the XSW method can be extended toward less perfect mosaic crystals such as perovskite oxides. We applied the XSW technique to study crystallographic positions of submonolayer of Pt deposited onto SrTiO<sub>3</sub> single crystals. The experiments were performed using a UHV MBE system installed on beamline 12ID-D at the Advanced Photon Source. The X-ray optics included an up-stream Si(111) L-N<sub>2</sub> cooled double-crystal monochromator, followed by a Si(004) channel-cut and a  $20 \times 100 \mu\text{m}^2$  slit. Using such a highly collimated, quasi-plane-wave, monochromatic and very narrow X-ray beam X-ray rocking curves close in width and shape to theory were measured from mosaic SrTiO<sub>3</sub>(001) substrates. The Pt was deposited onto a SrTiO<sub>3</sub>(001) surface prepared by combination of etching, annealing in oxygen and annealing in UHV. We studied the temperature dependence of the Pt position along the [001] direction. Different Pt positions for low (550-700°C) and high (800-950°C) annealing temperatures were found. We found also that the high temperature structure remains ordered after exposure to an open air environment. The off-normal XSW measurements revealed remarkable differences in Pt structure depending on coverage within submonolayer range.

#### 9:45 AM EE9.6

REAL TIME MEASUREMENT OF NANO-PARTICLE DIFFUSION IN THIN POLYMER FILMS BY X-RAY STANDING WAVES. Rodney Guico, Andrew Richter, Jin Wang, Advanced Photon Source, Argonne National Laboratory, Argonne, IL; Kenneth Shull, Dept of Materials Science and Engineering, Northwestern University, Evanston, IL.

Polymer/metal nanocomposites have emerged as an important research area due to their practical and fundamental significance in recent years. Much of the research in this field has focused on the diffusion properties of nanocomposites in bulk polymer matrices. In particular, it was found that the mobility of gold nano-particles was 2 to 3 orders of magnitude smaller than that predicted by Stokes-Einstein theory. Such a discrepancy was explained by the

mechanism related to the bridging between the particles through slow exchange kinetics of polymer segments at the polymer/metal interface. More recently, the viscosity of polymer melts at small scales has been reconsidered theoretically by Wyart & de Gennes. However, there have not been experimental data to verify these conclusions. In this work, we measured the diffusion of gold nano-particles in polymer thin films in real time during the polymer annealing processes above the polymer glass transition temperature. The profile of the metal particles perpendicular to the polymer surfaces was precisely determined by using x-ray standing waves (XSWs) generated during total external reflection. Previously, it has been demonstrated that the XSW method can be used to locate a heavy atom marker layer in thin films with angstrom spatial resolution. Here, the same method was utilized in a time-resolved manner thanks to the intense synchrotron x-ray beams and the strong gold L-fluorescence. Since the XSW technique is capable of probing the motion of the gold nanoparticles on the order of a few angstroms, the distribution of the particles can be measured before they start to coalesce. With the distributions measured precisely during the annealing, the diffusion coefficients of the gold nanoparticles have been determined at various annealing temperatures. The effect of the thin film thickness on the nano-particle diffusion properties is also discussed. Work supported by the U.S. DOE under Contract No. W-31-109-ENG-38.

#### 10:30 AM **EE9.7**

PROBING THE DEPTHS: INVESTIGATING THE DISTRIBUTION AND ORIENTATION OF SELF-ORGANIZED DOMAINS OF SOLUTION-PROCESSED CONJUGATED POLYMER FILMS AT BURIED INTERFACES. **Martin M. Nielsen**, Mourits Nielsen, Robert Feidenhans'l, Christian Kumpf and Klaus Bechgaard, Condensed Matter Physics and Chemistry Department, Risoe National Laboratory, DENMARK; Henning Siringhaus, Cavendish Laboratory, University of Cambridge, UNITED KINGDOM.

The transport properties of conjugated polymer thin films were recently shown [1] to depend strongly on the orientation of self-organized domains in the film. However, in Field Effect Transistor (FET) devices, the charge carriers are generated in a layer only a few nm deep near the gate-insulator/semiconductor interface, which in general is inaccessible to conventional techniques for structural characterization. Hence, it is crucial to develop new ways of characterizing this layer in order to gain further insight into the relationship between structure and mobility. In the present study, a depth-resolved grazing incidence diffraction method is demonstrated. A typical layered FET device, based on organic semiconducting material, consists of a semiconducting film on an insulating substrate. Using well-collimated X-ray synchrotron radiation it is possible to create a resonant coupling of the incoming and reflected X-rays, giving rise to X-ray standing waves of variable period, depending on the grazing incidence angle of the primary beam. Measuring the X-ray reflectivity of the sample allow a detailed modeling of the electric field throughout the film. The amplitude of the resonance enhanced X-ray standing wave field can be more than an order of magnitude larger than for the non-resonant case. Measuring the diffraction signal from self-organized domains for various distributions of the electric wave field intensities thus offers an attractive, non-destructive method for gauging their orientation and their distribution perpendicular to the interface.

[1] H. Siringhaus, P.J. Brown, R.H. Friend, M.M. Nielsen, K. Bechgaard, B.M.W. Langeveld-Voss, A.H.J. Spiering, R.A. Janssen, E.W. Meijer, P. Herwig, D.M. de Leeuw, Nature 401, 685 (1999).

#### 10:45 AM **EE9.8**

Transferred to **EE5.6**.

#### 11:00 AM **EE9.9**

INVESTIGATIONS OF BURIED INTERFACES USING HIGH ENERGY X-RAY REFLECTIVITY. **F. Rieutord**, J. Eymery, N. Boudet, D. Buttard, F. Fournel, CEA-DRFMC, Grenoble, FRANCE.

X-ray reflectivity using high-energy X-rays allows one to characterize interfaces between thick materials at nanometer scale. The technique combines the high penetration of X-rays allowing the crossing of the radiation through large thicknesses of material with the interface sensitivity of grazing angle techniques. In the case of a buried interface between two thick materials, the beam enters the sample through the side of one material and contributions of external surfaces are suppressed. Then, the technique is sensitive to the interface structure only. Examples are given using wafer bonding interfaces, both in the hydrophilic case (as used e.g. in Silicon-On-Insulator substrate fabrication) and in the hydrophobic case (Silicon/Silicon bonding).

#### 11:15 AM **EE9.10**

THIN FILMS AT THE WATER SURFACE STUDIED BY GRAZING INCIDENCE X-RAY DIFFRACTION. **Coralie Alonso**<sup>1</sup>, Ivan Kuzmenko<sup>1</sup>, Torben R. Jensen<sup>2</sup>, Kristian Kjaer<sup>2</sup>, Anne Renault<sup>3</sup>,

Meir Lahav<sup>1</sup>, Leslie Leiserowitz<sup>1</sup>. <sup>1</sup>Weizmann Institute of Science, Materials & Interfaces Dept., Rehovot, ISRAEL. <sup>2</sup>Matter Physics & Chemistry Dept, Risoe National Laboratory, Roskilde, DENMARK. <sup>3</sup>Groupe Matiere Condensee et Materiau, Universite Rennes, FRANCE.

Monomolecular films at the air-water interface can be investigated on the subnanometer scale with grazing incidence X-ray diffraction (GIXD) using synchrotron radiation. This technique utilizes the property of total external reflection of X-ray from a water surface for grazing angles: an evanescent wave generated within the film diffracts in the surface plane giving an image of the film reciprocal lattice. Three applications of GIXD are presented, making use of the synchrotron facilities at DESY (Hamburg, Germany) and at ESRF (Grenoble, France).

1. Long-chain cholesteryl esters (CE) deposited on the water surface spontaneously self assemble, forming crystalline interdigitated bilayers. The molecular organization was found to be similar to the 3D counterpart. Depositing CE in the presence of hydrocarbon additives yields to an 'interdigitated' monolayer comprising the CE and the additive. We plan to examine whether this result may mimic the inhibition effect of solvent on the growth of 3-D crystals with corrugated surfaces.

2. We have demonstrated that cholesteryl-*L*-glutamate forms a crystalline monolayer at the air-water interface within which the glutamate moieties are not closely packed. Thus, this system could specifically incorporate short amino acids from the subphase. Among several amino acids, *L*-leucine was found to dock in the voids between the glutamate moieties, and moreover this monolayer induces the formation of a crystalline bilayer of *L*-leucine by line epitaxy.

3. According to 2D diffraction theory, the shape of Bragg peaks is related to the mechanical constants of the film. Rigidity of the film can be deduced from a detailed peak analysis for primary and secondary short chain alcohols close to the melting temperature. Analysis shows a softening of the monolayer close to melting and moreover validates the use of synchrotron radiation to explore mechanical properties of thin films at the atomic scale.

#### 11:30 AM **EE9.11**

CHARACTERIZATION OF INTERFACIAL OXIDES BETWEEN DIELECTRIC THIN FILMS AND SILICON SUBSTRATE USING X-RAY REFLECTIVITY. **Sungdae Ji**, Changyong Park, Ki-Bong Lee, Dept of Physics and eSSC, POSTECH, Pohang, KOREA; Yong-Jun Park, Pohang Accelerator Laboratory, POSTECH, Pohang, KOREA; Sangbae Youn, Sujin Seo, Ho-Joung Kim, Soun-Young Lee, Hyundai Microelectronics, Cheongju, KOREA.

X-ray reflectivity intensities have been measured using synchrotron radiation with grazing incident scheme in order to characterize the structural properties of dielectric thin film stacks, including Ta<sub>2</sub>O<sub>5</sub>, on Si wafers after post-annealing in a variety of ambients. Interfacial SiO<sub>x</sub> layers formed during post-annealing are difficult to measure with conventional x-ray reflectivity analysis, due to low density contrasts of the layers to substrates comparing with high contrasts of top dielectric layers. Thicknesses of the interfacial SiO<sub>x</sub> layers have been estimated using Patterson function of density derivatives which can be obtained from Fourier transform of x-ray reflectivity curves normalized by Fresnel reflectivity of the substrates. Variations of the Patterson functions for different thermal ambients have been observed, and the results indicate changes in densities and thicknesses of the interfacial layers from their initial values.