

SYMPOSIUM R
Nanostructured Interfaces

April 2 – 4, 2002

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SESSION R1: CHARACTERIZATION OF
NANOSTRUCTURED INTERFACES

Chair: Gerd Duscher
Tuesday Morning, April 2, 2002
Salon 5/6 (Marriott)

8:30 AM *R1.1

INTERFACES IN NANOSTRUCTURED MATERIALS.

Manfred Ruehle, Max-Planck-Institut fuer Metallforschung, Stuttgart, GERMANY.

The density of interfaces is high in nanostructured materials. It is crucial to identify not only the different components of the nanostructured materials but also the structures and compositions of the different interfaces. In nanostructured materials the length scale in at least one dimension ranges in the nanometer scale. Those materials consist either of layered structured films (1 D-nanoscale materials), rod-like structures (2 D) or fine grain materials (3 D). The microstructure of the materials requires firstly the identification of the different phases in existing materials. This can be done by energy-filtering transmission electron microscopy (EFTEM). A quantitative evaluation of the strains in the different constituents can be done by convergent beam electron diffraction (CBED). Of great interest is, however, the analysis of the structure and composition of internal interfaces. Those defects often control the properties of a material. In contrast to the study of external interfaces and surfaces there exist only a very limited number of experimental techniques for the characterization of internal interfaces. X-ray scattering experiments and transmission electron microscopy (TEM) are the most important ones. In this paper advances in the different TEM techniques will be described. Recent results on quantitative high-resolution transmission electron microscopy (HRTEM) and quantitative analytical electron microscopy (QAEM) studies will be reported. Detailed electron energy loss spectroscopy (EELS) studies reveal information on electronic bonding, coordination number and distance to neighboring atoms. In the presentation results will be discussed on the different nanostructured materials.

9:00 AM R1.2

QUANTITATIVE NANOMETER-RESOLUTION MAPPING OF COMPOSITION AND BONDING AT INTERFACES BY ANALYTICAL ELECTRON MICROSCOPY. J. Bentley, Oak Ridge National Laboratory, Metals and Ceramics Division, Oak Ridge, TN.

Structure-property correlations in a range of nanostructured materials, with an emphasis on interfaces, have been studied with the use of analytical electron microscopy methods for mapping composition and bonding at nanometer resolution. Elemental mapping by energy-filtered transmission electron microscopy (EFTEM) has been employed extensively; a critical aspect has involved development and optimization of reliable methods to yield fully quantitative composition maps. Issues involve dealing with the problems of overlapping edges and sensitivity for low concentrations. The EFTEM methods have been extended to energy-loss fine structure mapping for chemical rather than elemental information. The acquisition in the scanning transmission electron microscopy (STEM) mode of simultaneous energy-dispersive X-ray (EDS) and electron energy-loss (EELS) spectrum images is a powerful alternative to EFTEM. However, spectrum lines acquired in the TEM mode with an imaging filter can be an attractive alternative to STEM mode spectrum lines, especially for energy-loss fine structure studies of interfaces. EFTEM and STEM methods have been extensively applied to Co-Cr-Pt-Ta-B longitudinal magnetic recording media, where intergranular Cr and B segregation is critical for the magnetic isolation of the typically <20 nm diameter grains necessary for optimum magnetic recording performance. EFTEM elemental mapping of clusters of silica and titania nanoparticles has revealed important information on incomplete mixing during the processing of these model systems for explosives. EFTEM and STEM mode mapping of 3d transition metal L-edge white line intensities have been used to produce valence-state maps in TM oxide nanostructures and to explore the magnetic state of segregated grain boundaries in Co-based recording media. Finally, TEM spectrum lines and EFTEM elemental mapping of liquid-phase sintered silicon nitride ceramics have revealed important differences in composition between the ~1-nm wide amorphous intergranular films and the larger glass pockets at triple points. Research at the Oak Ridge National Laboratory SHaRE Collaborative Research Center was sponsored by the Division of Materials Sciences and Engineering, U.S. Department of Energy, under contract DE-AC05-00OR22725 with UT-Battelle, LLC.

9:15 AM R1.3

QUANTITATIVE HRTEM INVESTIGATION OF AN OBTUSE DISLOCATION REACTION IN GOLD WITH A Cs CORRECTED FIELD EMISSION MICROSCOPE. J.R. Jinschek, C. Kisielowski, T. Radetic, U. Dahmen, National Center for Electron Microscopy (NCEM), Lawrence Berkeley National Lab. (LBNL), Berkeley, CA; M.

Lentzen, A. Thust, K. Urban, Forschungszentrum Jülich GmbH, Jülich, GERMANY.

Nowadays material science benefits from high-resolution transmission electron microscopy (HRTEM) with a resolution that extends to the information limit of field emission microscopes that can reach into the sub Angstrom region. The procedure involves a reconstruction of the electron exit wave from a focal series of images or imaging with a Cs corrected microscope. We utilized a CM200 FEG instrument equipped with a Cs corrector [1] to investigate quantitatively the core structure of an obtuse dislocation reaction in gold. A determination of the structure from a single lattice image is compared with the result from an exit wave reconstruction. Quantitative information is obtained by extraction of the column positions surrounding the dislocation core with precision on a pm level. Moreover, it is shown that the large scattering power of the gold atoms (atomic number $z = 79$) can be utilized to extract the number of gold atoms in individual atomic columns from reconstructed electron exit-waves of wedge shaped samples. A comparison of multi-slice calculations with experiments gives guidelines on how resolution affects the limit as to which the number of atoms in a particular column can be determined from a phase change of the electron exit wave. Since the magnitude of the phase change oscillates with sample thickness and depends on resolution, it is principally possible to probe the information limit of an electron microscope through the maximum phase change that occurs on a wedge shaped sample.

[1] M. Haider, H. Rose, S. Uhlemann, E. Schwan, B. Kabius, K. Urban, Ultramicroscopy 75 (1998) 53.

9:30 AM R1.4

ANALYSIS OF GIBBSIAN SEGREGATION AT HETEROPHASE INTERFACES USING ANALYTICAL TRANSMISSION ELECTRON MICROSCOPY: A NOVEL APPROACH. B.J. Kooi, S. Mogck, O. Wouters, J.Th.M. De Hosson, Dept. Applied Physics, University of Groningen, Groningen, THE NETHERLANDS.

Recently, we proposed a novel approach to measure Gibbsian segregation at heterophase interfaces using analytical TEM that offers advantages over approaches that are also applicable to grain boundaries [1]. The method allows quantification of the concentrations in a monolayer (ML) at the interface and the results are less sensitive to drift and more reliable for quantification than the results of a line-scan or mapping. Compared to the use of a scan raster, the present approach shows an improved detection sensitivity. The requirement for the method is that at the A(B)/C(B) interface the solvent A (or C) shows an abrupt and significant change in concentration at the interface to which solute B may segregate. The experimentally obtained concentration of solute B is plotted as a function of solvent A (or C) and compared with simulated results having as input parameters concentration of B in solvent A and C and in the ML at the interface and the full-width-half-maximum of the electron probe. The method is applied to the possible segregation of indium to parallel {111} Cu/MnO interfaces. The indium concentration in the Cu matrix is 3.8 ± 0.4 at.% on average and In (and Cu) atoms do not dissolve in the MnO precipitates. A concentration of 15 ± 3 at.% In was obtained for the terminating Cu {111} layer at the interface. On the basis of a comparison between experimental HRTEM images of the interface, atomistic calculations and image simulations it is concluded that indium atoms in this layer segregate to generalized O nodes present in-between the dislocation lines of a trigonal misfit-dislocation network with $\{110\}$ line direction and $1/6\langle 112 \rangle$ Burgers vectors. On theoretical grounds a favourable indium concentration at the interface of 14 ± 7 at.% is estimated which compares well with the experimental findings.

[1] B.J. Kooi, O. Wouters, J.Th. M. De Hosson, Acta Mater., Accepted Oct. 2001.

SESSION R2: NANOSTRUCTURED INTERFACES IN
CATALYSTS AND SENSORS

Chair: Gerd Duscher
Tuesday Morning, April 2, 2002
Salon 5/6 (Marriott)

10:15 AM *R2.1

THERMAL STABILITY AND AGING MECHANISMS OF HIGH-TEMPERATURE AUTOMOTIVE CATALYSTS. X.Q. Pan and H.P. Sun, Department of Materials Science and Engineering, University of Michigan, Ann Arbor, MI; G.W. Graham and R.W. McCabe, Ford Research Laboratory, Dearborn, MI.

Improvements in the thermal stability of three-way automotive catalysts are sought because they should lead to lower emissions and better fuel economy. A major advance in this area came from the recent development of high-surface-area ceria-zirconia. It is well known that both the metal and the oxide support undergo sintering

under redox aging conditions, a fraction of the metal particles that become trapped within the ceramic matrix. In the present work, we studied the aging process of oxide-supported automotive exhaust catalysts. The model catalytic materials at different aging stages were investigated by high resolution transmission electron microscopy, analytical electron microscopy techniques, in combination with other supporting analyses. We have directly observed a catalyst deactivation phenomenon, the deep encapsulation of precious metal by ceria-zirconia support material during high-temperature accelerated aging. It was found that the metal particles initially become loosely trapped within the ceria-zirconia before it finally collapses around them to create a fully dense composite. Consequently, before this stage is reached, even more Pd may be lost to catalysis than previously thought. The relationships between the microstructural evolution of catalysts during the aging process and the physical and chemical properties measured in the same catalyst materials will be discussed.

10:45 AM R2.2

ELECTRON HOLOGRAPHIC NANO-CARACTERIZATION OF GOLD CATALYST AT INTERFACE. Satoshi Ichikawa, Tomoki Akita, Mitsutaka Okumura, Koji Tanaka, National Institute of Advanced Industrial Science and Technology, AIST Kansai, Osaka, JAPAN; Masatake Haruta, National Institute of Advanced Industrial Science and Technology, AIST Tsukuba, Ibaraki, JAPAN.

The catalytic properties of nanostructured gold catalyst are known to depend on the size of the gold particles and to be activated when the size of them decreases down to a few nanometers. We investigated the size dependence on the three-dimensional nanostructure and the mean inner potential of the gold catalysts supported on titanium oxide by the electron holography and the high-resolution electron microscopy (HREM). The contact angle of the gold particle on the titanium oxide tends to be over 90 degrees in case of the gold particles with the size over 5nm, and it tends to be below 90 degrees in case of with the size below 2nm. This change of the morphology (the decrease of the contact angle) causes to increase the area of the interface and the perimeter between the gold and titanium oxide support, which is considered to be an active site for CO oxidation. The mean inner potential of the gold particles also changed when the size of them decreased. The value of the inner potential of gold, which is about 25V in bulk state, becomes over 40V when the size of the gold particle is under 2nm. This phenomenon indicates the existence of the charge transfer at the interface between gold and titanium oxide. The 3-D structure change and the inner potential change should be attributed to the specific electronic structure at the interface, owing to both the "nano size effect" and the "hetero-interface effect".

11:00 AM R2.3

NOVEL PHYSICAL AND CHEMICAL PROPERTIES OF Ni FILMS AT MONOLAYER THICKNESS. Neetha A. Khan, Sergey Rykov, Jinguang G. Chen, University of Delaware, Dept of Materials Science and Engineering, Newark, DE.

Bimetallic interfaces have been shown to have unique physical and chemical properties in comparison to the pure metals in the fields of catalysis, electrochemistry and materials science. Previous studies have indicated that the formation of a metal-metal bond at the interface changes the physical and electronic properties of the metal atoms on the surface, in particular at monolayer thickness. Our goal is to develop physical and chemical probes to determine whether and how the monolayer film differs from bulk films. In this study, we have used surface science techniques to investigate the properties of Ni films that are grown epitaxially on the single crystal substrates of Pt(111) and W(110). Using single crystals, we can prepare well-defined bimetallic surfaces in an ultrahigh vacuum chamber. We have used NEXAFS (Near-Edge X-ray Absorption Fine Structure) and XPS (X-ray Photoelectron Spectroscopy) to characterize the electronic properties of this surface. These experiments indicate that there is little difference in the electronic properties between monolayer and thick Ni films. Despite this, we have still observed unique chemical properties on the monolayer Ni film by using small organic molecules such as cyclohexene and thiophene as chemical probes. These molecules show a novel low-temperature reactivity towards hydrogenation and hydrodesulfurization. These results illustrate that chemical probes can be more sensitive to the unique properties of bimetallic interfaces than spectroscopic methods.

11:15 AM R2.4

THE SURFACE INTERFACE CHARACTERISTICS OF VERTICALLY ALIGNED CARBON NANOTUBE AND GRAPHITIC CARBON FIBER ARRAYS GROWN BY THERMAL AND PLASMA ENHANCED CHEMICAL VAPOR DEPOSITION. Lance Delzeit, NASA Ames Research Center, Moffett Field, CA; Cattien V. Nguyen, Jun Li, Jie Han, ELORET Corporation, Sunnyvale, CA; M. Meyyappan, NASA Ames Research Center, Moffett Field, CA.

The development of nano-arrays for sensors and devices requires the growth of arrays with the proper characteristics. One such application is the growth of vertically aligned carbon nanotubes (CNTs) and graphitic carbon fibers (GCFs) for the chemical attachment of probe molecules. The effectiveness of such an array is dependent not only upon the effectiveness of the probe and the interface between that probe and the array, but also the array and the underlying substrate. If that array is a growth of vertically aligned CNTs or GCFs then the attachment of that array to the surface is of the utmost importance. This attachment provides the mechanical stability and durability of the array, as well as, the electrical properties of that array. If the detection is to be acquired through an electrical measurement, then the appropriate resistance between the array and the surface need to be fabricated into the device. Data on the growth of CNTs and GCFs from both thermal and plasma enhanced chemical vapor deposition will be shown. The focus will be on the characteristics of the metal film from which the CNTs and GCFs are grown and the changes that occur due to changes within the growth process.

11:30 AM R2.5

NANOSTRUCTURED POLYMER BRUSHES WITH REVERSIBLY CHANGING PROPERTIES. Denis Usov, Manfred Stamm, Sergej Minko, Christian Froeck, Institut fuer Polymerforschung Dresden, Dept Physical Chemistry and Physics of Polymers, Dresden, GERMANY; Andreas Scholl, Lawrence Berkley Natl Lab, Berkley, CA; Markus Mueller, Johannes Gutenberg Universitaet, Institut fuer Physik, Mainz, GERMANY.

Polymers may be grafted at different densities to a solid surface to form brushes of different extension. Utilizing two incompatible polymers, which are grafted statistically, offers interesting surface properties: the lateral and perpendicular organization might reversibly change in different environments in a controlled way. The surface of mixed brushes thus can provide hydrophilic or hydrophobic behaviour after dipping in preferential solvents and subsequent drying. Lateral nanostructures are investigated by scanning force microscopy, while chemical nanoheterogeneity is studied by photoelectron emission microscopy. The competition of lateral versus perpendicular segregation causes structures, which are revealed also by computer simulations of mixed brushes.

11:45 AM R2.6

SURFACE MODIFICATION OF VERTICALLY ALIGNED CARBON NANOTUBE ARRAY AND CHEMICALLY OPENING TIP ENDS FOR COVALENT ATTACHMENT OF DNA MOLECULES. Cattien V. Nguyen, James Kaysen, Jie Han ELORET Corporation/NASA Ames Research Center, Moffett Field, CA; Lance Delzeit, M. Meyyappan NASA Ames Research Center Moffett Field, CA.

To realize the potential of carbon nanotube as nanowire for application in biosensor, chemical coupling to molecular recognition molecules, like DNA and proteins, must first be demonstrated. To this end, a vertically aligned carbon nanotube array with tips exposed at the surface-air interface was fabricated. Filling the gaps between carbon nanotubes to the top of the surface of the array with a spin-on film of siloxane derivative modified the hydrophobic nature of the nanotube surface. Scanning electron micrograph showed that the exposure of the nanotube tip ends could be controlled to a high degree by adjusting parameters such as height of the nanotube and/or film thickness. Air oxidation at 430°C and subsequent strong acid oxidation removed iron catalysts at the tips and chemically open the ends of carbon nanotubes. Preliminary results from chemical coupling of DNA molecules to the open ends of carbon nanotubes in the fabricated array are presented.

SESSION R3: NANOSTRUCTURED INTERFACES IN STRUCTURAL MATERIALS

Chairs: Yimei Zhu and Alexander V. Kvit
Tuesday Afternoon, April 2, 2002
Salon 5/6 (Marriott)

1:30 PM *R3.1

FIRST-PRINCIPLES STUDY OF THE STRUCTURE AND TENSILE STRENGTH OF POLAR AND NON-POLAR INTERFACES OF A SiC GRAIN BOUNDARY. Masanori Kohyama, Green Life Tech., National Inst. Adv. Ind. Sci. & Tech., Ikeda, Osaka, JAPAN.

The effects of C-C and Si-Si wrong bonds and of interface stoichiometry to determine polar and non-polar interfaces should be of great importance for the nano-scale design of SiC grain boundaries. In this paper, we examine such effects on the atomic and electronic structure and on the tensile strength and fracture of a SiC coincidence boundary by using the *ab initio* pseudopotential method based on the

density-functional theory (DFT). We deal with the $\Sigma=9$ coincidence boundary in cubic SiC. The N-type and P-type polar interfaces contain C-C and Si-Si wrong bonds, respectively, and the non-polar interface contains both type of wrong bonds. All the interfacial bonds are well reconstructed with relatively small bond distortions, and the wrong bonds have features rather similar to bulk diamond and Si bonds. The relative stability among the three interfaces with different stoichiometries has been analyzed theoretically as a function of atomic chemical potentials. The electronic-structure changes associated with the wrong bonds have been analyzed in detail. Calculated results have been compared with HRTEM and EELS observations [1]. Then we have examined the tensile strength and fracture of these interfaces through *ab initio* tensile test [2]. In this test, tensile strength and fracture of each interface are examined through the behavior of electrons and ions based on the DFT by applying tensile strain in a small increment. We have found that the reconstructed interfaces have rather high tensile strength comparable to bulk crystal, and we have observed the critical bond stretching for Si-C bond breaking. It has been shown that the atomic-scale inhomogeneity associated with the wrong bonds have serious effects on the tensile strength and fracture.

[1] K. Tanaka and M. Kohyama, "Grain Boundary Engineering in Ceramics", T. Sakuma et al. (ACerS, 2001), p.231.

[2] M. Kohyama, Phil. Mag. Lett. 79 (1999) 659.

2:00 PM *R3.2

MECHANICAL BEHAVIOUR OF METALLIC NANOSTRUCTURES RELATED TO GRAIN-BOUNDARY STRUCTURE.

Yannick Champion, Sandrine Guerin-Mailly, Cyril Langlois, Martin Hytch, CECM-CNRS, Vitry-sur-seine, FRANCE; Patrick Langlois, LIMHP-CNRS, Univ Paris XIII, Villetanneuse, FRANCE.

Understanding the mechanical behaviour of metallic nanostructures is a key issue for their development. On the one hand, knowledge of the plastic behaviour at various temperatures is essential to control the synthesis, forming, and machining of such materials. On the other hand, a clear understanding of atomic and mesoscopic mechanisms, involving defects and their interactions, is essential for the control of ageing and functional properties. Regarding plastic deformation at room temperature, there is now evidence for unusual behaviour in nanostructured metals. In addition to high tensile strength and extended elongation, tensile tests reveal nearly perfect elasto-plastic deformation. Such behaviour was initially attributed to grain-boundary sliding. However, intergranular areas (including triple junctions) may possess special properties compared to their microcrystalline counterparts. For example, low activation energies have been measured for grain-boundary diffusion and it has been observed that grain-boundaries may act as dislocation sources and nucleation sites for deformation twinning. In this presentation, we report on analysis on copper bulk nanostructures. Properties of grain-boundaries are studied, by cross-correlating information from mechanical tensile testing and structural analysis, including X-ray diffraction and transmission electron microscopy (TEM). Macroscopic bulk specimens (with grain size of about 80 nm) are prepared by powder metallurgy techniques, modified to fit to the special properties of nanocrystalline powders. Processing includes cold-isostatic pressing, sintering and differential extrusion. The powders used (grain size of 40 nm) are synthesised by evaporation and cryo-condensation of a metallic vapour within liquid nitrogen. Results on mechanical testing and structural analysis will be reported. Emphasis will be placed on the structure of grain boundaries (type of grain-boundary, grain-boundary thickness and atomic structure) studied by TEM and high resolution TEM image analysed using the phase image technique. These observations will then be related to the unusual mechanical true stress-true strain curves of the metallic nanostructures.

2:30 PM R3.3

GREEN'S FUNCTION METHOD FOR CALCULATING STRESS AND STRAIN FIELDS DUE TO QUANTUM DOTS IN III-V SEMICONDUCTORS. Vinod Tewary, Materials Reliability Div, NIST, Boulder, CO.

A new elastostatic Green's function method is described for calculating three dimensional stress and strain fields due to quantum dots in III-V semiconductors. The Greens function method includes the full effect of the elastic anisotropy and the presence of interfaces and free surfaces, and is applicable to quantum dots of arbitrary shapes and compositions. The method gives results in a semi-analytical form that is suitable for parameterization and interpretation of experimental results in contrast to purely numerical techniques that are CPU intensive and hence not convenient for parametric analysis of experimental results. The previous analytical and semi-analytical methods of stress analysis near quantum dots either assumed the semiconductor to be elastically isotropic or used a series expansion in the anisotropy parameter. The series representation suffers from problems of convergence and is applicable only to semiconductors with small anisotropy. Moreover, the previous

analytical methods either neglected or crudely approximated the effect of the interfaces and free surface. Elastic anisotropy is very important for strain-field interaction between the quantum dots and their interaction with the free surface which determines the further growth and ordering of quantum dots. We use the newly developed delta-function representation of the anisotropic Green's function in the slowness space that is computationally very efficient. The effect of the finite thickness of the caplayer is included by imposing zero-traction boundary condition at the free surface. Continuity conditions are imposed at the interface. Numerical results for the stress and the strain field around the quantum dots and at the surface of the epilayer above a seed layer of dots are presented for the InAs/GaAs system.

2:45 PM R3.4

INTERFACE CHEMICAL STRUCTURE AND ELECTRONIC STRUCTURE OF HIGH PURITY SiC. Eriko Takuma, Hideki Ichinose, the Univ of Tokyo, Dept of Materials Science, Tokyo, JAPAN; Masanori Kohyama, AIST Kansai, Special Division of Green Life Tehnology, Osaka, JAPAN.

Interface chemical structure in atomic dimension of both high purity α (6H) and β (3C) silicon carbide (SiC) was investigated by our atomic resolution high voltage transmission electron microscope (ARHVTEM). Silicon and carbon in the interface was directly distinguished from each other by the image contrast at the optimum defocus condition. The structure of this interface was similar to the lowest energy grain boundary of 6H type SiC in periodicity[1]. The rotation angle was 70.5 degrees around common $\langle 11\bar{2}0 \rangle$ axis. The interface consisted of 5-7-6-6-6-6-membered rings, showing zigzag shape. A half part of the period was parallel to (111) plane of 3C structure and to (1 $\bar{1}$ 02) plane of 6H structure and the other half part of the period was to (115) and (1 $\bar{1}$ 02). There was an atomic pair of same element and were two three-fold coordinated atoms in one period. All of other atomic pairs consisted of unlike element. The three-fold coordinated atomic sites were occupied by carbon and an atomic species of the same elemental pair was Si. The concluded structure is the same as the one which is recognized to be the lowest energy structure of SiC grain boundary[2]. The first-principle molecular dynamics calculation of this boundary supported the experimental atomic structure. The calculation revealed that this boundary showed several particular energy states in the band-gap of SiC crystal. The gap states were shown to be localized at the three-fold coordinated C atoms in the boundary.

[1] E. Takuma and H. Ichinose, Mat. Res. Soc. Symp. Proc., 652 (2000).

[2] E. Takuma and H. Ichinose, Philo. Mag. A, to be published.

3:30 PM *R3.5

IN-SITU TEM OBSERVATION OF SOLID-LIQUID INTERFACES. H. Saka, Nagoya University, Dept. of Quantum Engg., Nagoya, JAPAN.

Solid-liquid interfaces are observed using in situ heating experiment in a transmission electron microscope. Interfaces observed include S/L interface in aluminum, alumina, those between solid Si and liquid Al, eutectic alloys, solder joint and galvanizing.

4:00 PM R3.6

DEWETTING OF ULTRATHIN PT FILMS AND EMBEDDING OF PT NANOPARTICLES INDUCED BY ION IRRADIATION. Xiaoyuan Hu, David G. Cahill, Robert S. Averback, Dept of Materials Science and Engineering, Urbana, IL; Robert C. Birtcher, Argonne National Laboratory, Argonne, IL.

Effects of heavy ion irradiation on the structure of metal/dielectric interfaces are studied in real-time using in situ transmission electron microscopy. Ultrathin Pt films dewet from SiO₂ or C substrates for 800keV Kr⁺ ion doses between 10¹⁴ cm⁻² and 6x 10¹⁵ cm⁻². Fissures in the as-deposited films act as the nuclei for dewetting. The evolution of fissures includes filling in of small fissures (< 1x 10¹⁴ cm⁻²) as well as growth and coalescence (> 1x 10¹⁵ cm⁻²) of large fissures. We characterize the growth kinetics of the fissures and the receding velocity of the contact lines by measuring the area and width of individual fissures as functions of dose. The contact lines move at a velocity of 0.02-2 m/s. At doses of ~ 1x 10¹⁶ cm⁻², isolated Pt nanoparticles form and become embedded in the SiO₂ substrates; capillary forces are the driving force for ion induced embedding. We study the kinetics for the embedding of Pt nanoparticles using cross sectional transmission electron microscopy. The velocity of embedding is only weakly dependent on particle size. For particle diameters between 5-20 nm, the velocity of embedding decreases with increasing ion dose, finally becoming zero at ~ 1x 10¹⁶ cm⁻² when the particles are fully embedded in the substrate. The rate of embedding is consistent with past studies of irradiation-induced viscous flow of SiO₂. Sinking of Pt particles is inhibited, however, for crystalline substrates such as Al₂O₃.

R4.1
INTERFACIAL NATURE OF UNPROTECTED PLATINUM
NANOPARTICLES IN ORGANIC MEDIA. Yuehua Chen, Hanrui
Guo, Peking Univ, Dept of Chemistry, Beijing, PR CHINA.

Many new technologies will be enhanced by the ability to control the structure of materials on a nanometer-length scale. Colloidal metal nanoparticles are of great interest because of their applications in optical, electric and magnetic devices, and their use as catalysts, absorbents, and sensors. Nanoparticles are also ideal building block for self-assembled superlattice structures and other nanostructured materials. Recently, a new method for the preparation of stable platinum nanoparticles in the absence any usual protective agent in organic media has been reported. This kind of metal nanoparticles can be easily transformed to various protected nanoparticles with the same metal core. Hence, these stable nanometer scale building blocks provide new opportunities for preparing many functional materials. But little is known about the chemical composition and bonding at the interfaces of the 'unprotected' nanoparticles. The goals of this paper are 3-folds: (1) Using proton NMR, FT-IR and element analysis to provide more detailed structural characterization at the interfaces of the 'unprotected' Pt nanoparticles in organic media. (2) From the findings of the characterization to develop a deeper understanding of the high stability of the 'unprotected' Pt nanoparticles. (3) To transform the 'unprotected' Pt nanoparticles to the PPh-3 Capping Pt nano-particles, ³¹P NMR and FT-IR results reveal that the possibility of change at the interfaces of the unprotected Pt nanoparticles. The results will be described and discussed in this paper.

R4.2
MICROSTRUCTURE CHARACTERIZATION AND MAGNETIC
PHASE TRANSITION OF LAYERED HEXAGONAL Ni-S
NANOCRYSTALS. Xiang-Cheng Sun, J. Antonio Toledo, Prog.
Molecular Simulation, Instituto Mexicano del Petróleo (IMP), DF
Mexico, MEXICO; J. Reyes-Gasca, Institute of Physics, National
University of Mexico (UNAM), DF Mexico, MEXICO.

Nickel sulfides (Ni-S) has been the subject of consideration interest for several years because it exhibited metal-insulator and magnetic phases transition. In addition, novel Ni-S materials can be used as a hydrosulfurization catalyst and in solar storage to absorb solar energy. In the present study, layered nickel-sulfides (Ni-S) nanocrystals had been successfully prepared by low-temperature hydrothermal approach. Rietveld X-ray diffraction (XRD) analysis indicated those layered Ni-S materials were typical hexagonal structure (NiAs-type) with space group of P63/mmc. It is interested that to note the selected area electron diffraction (SAED) patterns give good evidence of hexagonal superlattice. X-ray energy dispersive spectra (XEDS) reveal that there are two hexagonal form nanocrystals that corresponded to NiS_{1.03} and NiS nanophases, respectively. High-resolution transmission electron microscopy (HREM) lattice images confirm that those are lamellar domain nanostructures with hexagonal superlattice. In particular, all the simulated HREM images were in good agreement with the observed HREM lattice images. Especially, the simulated SAED patterns that based from hexagonal Ni-S crystallographic model were showed to match well with the experimental SAED patterns which taken from crystal plane along <11.0>, <10.1> and <10.0> zone axes. Magnetization (susceptibility) measurements for those Ni-S nanocrystals were performed by using a SQUID magnetometer. The first-order magnetic phase transition, from Pauli-paramagnetic phase (PM) to the antiferromagnetic ordering (AFM), had been exhibited. Above the magnetic phase transition temperature, Curie-Weiss type susceptibility was found. It was suggested, microstructure features of this kind of hexagonal Ni-S nanocrystal provide good evidence that is related to this magnetic phase transition.

R4.3
PROPERTIES OF ZINC OXIDE NANO-PARTICLES COATED
WITH ALUMINUM. Yuan Fangli, Huang Shulan, Li Jinlin, Chen
Yunfa, Inst of Process Engr, Chinese Acad of Sci, Beijing, CHINA.

Zinc oxide nano-particles have been paid more attention for their unique properties, but the high catalytic activity restricts their application. Particle surface modification is regarded as one of the effective way to restrain their high catalytic activity. In this paper, zinc oxide nano-particles coated with aluminum have been prepared by conducting the aluminum precipitation on the precursor basic zinc carbonate(BZC) of zinc oxide. The slurry of BZC white precipitation was obtained by ZnSO₄ solution adding to the NH₄HCO₃ solution

under stirring. Next, Al₂(SO₄)₃ and NH₄HCO₃ solution were precipitated onto the BZC surface. After filtered, washed and dried, zinc oxide nano-particles coated with aluminum were prepared by calcining the composite precipitation powders at 600° for 1 hour. TEM shows that the zinc oxide particles coated with aluminum are bigger than that without coated. There is a homogeneous film formed on the zinc oxide nano-particle surface, and the coated particle size is about 50-60nm. The thickness of the layer estimated by high magnification transmission electronic micrography is about 4-5nm. X-ray diffraction and lattice fringes data show that coated aluminum turns into surface ZnAl₂O₄ phase by means of reaction between zinc oxide and aluminum. The aluminum coating is effective in reducing the catalytic activity of zinc oxide nano-particles. The results show that zinc oxide particles have lower oxidation catalytic and photocatalytic activities. Zinc oxide nano-particles coated with aluminum not only keep in high effect in absorbing UV radiation, but also suppress the form of the yellow coloration. As a result the coated zinc oxide powders turn to white color from pale yellow color of resulting powders produced by this wet chemical route.

R4.4
CONTROL OF HYDROPHOBICITY OF ACTIVATED CARBON BY
SELF ASSEMBLY MONOLAYERS FOR ADSORPTION REMOVAL
TRIHALOMETHANES IN WATER. Akihide Shirotori, Seimei
Shiratori, Keio Univ, Dept of Applied Physics & Physico-Informatics,
Yokohama, JAPAN.

Recently, it has been the problem that Trihalomethanes "THMs" in tap water have a bad influence on human health. They are the materials produces after the reaction between chlorine used for disinfection and a little organic materials in water. They are the chemical structure replaced three hydrogen of methane(CH₄) with halogen elements (fluorine=F, chlorine=Cl, iodine=I). There is doubt that chloroform and bromodichloromethane are carcinogenic substances. The maximum allowable level of total THMs in tap water was decided by the Ministry of Health and Welfare of U.S.A. and Japan at 0.1mg/L. Among individual THM, that for chloroform, bromodichloromethane, dibromochloromethane and bromoform is set at 0.06, 0.03, 0.1, and 0.09mg/L, respectively. In order to remove the carcinogenic substances from tap water, high performance and long life filters were strongly required. In this study, we succeeded in changing the nano composition of the surface and pore structures on Activated Carbon (AC) by controlling the hydrophobicity of the surface and nanoscale pore of AC. To fabricate the new type of AC, it was treated by silane coupler to form self assembly monolayers on the surface. The remarkable characteristics of the new AC were proved from the experimental data from the B.E.T. surface area measurement pore size distribution measurement. Contact angle measurement and XPS analysis. We confirmed these high hydrophobic AC had high adsorption and removal characteristics for the toxic substances as compared with as-received AC because we consider that the affinity between AC and THM improved by improving hydrophobicity of ACD.

R4.5
CURRENT TRANSPORT OF MULTI-WALLED CARBON
NANOTUBES UPON THE ADSORPTION OF THIOL-
CONTAINING MOLECULES. Chang Soo Lee, Whikun Yi, Taewon
Jeong, Jeonghee Lee, Jungna Heo, SeGi Yu, Won Seok Kim*, Ji-Beom
Yoo**, Young Hee Lee*, and J. M. Kim, The National Creative
Research Initiatives, Center for Electron Emission Source, Samsung
Advanced Institute of Technology, Suwon, KOREA. *Department of
Physics, Sungkyunkwan University, Suwon, KOREA. **Center for
Nanotubes and Nanostructured Composite, Sungkyunkwan
University, Suwon, KOREA.

The electron transport of a single multi-walled carbon nanotube (MWNT) was investigated upon the adsorption of organic molecules, such as dodecanol, dodecanethiol, and benzenethiol. MWNTs grown by thermal chemical vapor deposition on the nickel-catalyzed silicon substrate were used for this experiment after dispersing in ethanol. A droplet of the MWNT-dispersed solution was coated and dried on a gold patterned silicon substrate. A MWNT was electrically bridged to patterned gold leads. A gold patterned substrate was transferred to the vacuum chamber for the adsorption of organic molecules and current-voltage (I-V) measurement. The adsorption of a thiol-containing molecules on a MWNT was performed by releasing a thiol vapor from the container to the vacuum chamber through a needle valve to reach a certain pressure level. I-V curve remained unchanged for the adsorption of dodecanol, whereas, the current increased from 2.4 (before adsorption) to 6.5 μ A with the increase in vapor pressure of dodecanethiol up to 3.2 mbar, and also current increased from 1.66 (before adsorption) to 9.56 μ A with increasing vapor pressure of benzenethiol. Considering the fact that most electrons flow through the outmost shell of a MWNT, the adsorption of dodecanethiol or benzenethiol molecules may influence the electron transport within the MWNT by the formation of an electron conducting channel through

exchange of electrons between the MWNT and adsorbed thiol molecules.

R4.6

UV-INDUCED ATTACHMENT OF POLYMER ULTRATHIN FILMS AND CREATION OF NANOSTRUCTURES ON SILICON WAFERS. Bernadette Harnish, Michele Bartlett, Jinah Chung, Mingdi Yan, Portland State Univ., Dept of Chemistry, Portland, OR.

We found that ultraviolet irradiation resulted in attachment of nanometer thick polymer thin films on silicon wafers. The procedure consisted of spin-coating a polymer film onto a silicon wafer and irradiating the film with UV light. Following solvent extraction, a fairly robust film remained. The thickness of the films, varied from a few nanometers to over a hundred nanometers, were controlled by changing the concentration of the polymer in solution and the molecular weight of the polymer used. This simple process has been used to successfully adhere polystyrene (PS), polyvinylpyrrolidone (PVP), and poly(vinylchloride) (PVC) to the surface of silicon wafers. The photochemical nature of this method also allowed for the fabrication of patterned polymer films on silicon wafers by way of photolithography. The result was the formation of spatially defined polymer microstructures that can easily be visualized with AFM. The mechanism by which the polymer thin films adhere to silicon wafers will be investigated.

SESSION R5: POSTER SESSION
STRUCTURAL MATERIALS
Tuesday Evening, April 2, 2002
8:00 PM
Salon 1-7 (Marriott)

R5.1

A DISLOCATION-BASED APPROACH FOR UNDERSTANDING GRAIN BOUNDARY DISSOCIATION. D.L. Medlin, D. Cohen, G. Lucadamo, Sandia National Laboratories, Livermore, CA; S.M. Foiles, Materials and Process Modeling Department, Sandia National Laboratories, Albuquerque, NM.

Grain boundaries in low stacking-fault-energy metals often spread into a nanometer-scale, three-dimensional configuration composed of a dense array of stacking faults. This behavior is of particular relevance for nanostructured materials because of the increased volume fraction of material associated with interfaces and because the constraints of geometric compatibility in such small-grained systems can locally promote or retard the dissociation. In this presentation, we discuss a dislocation-based approach for predicting the structures of dissociated boundaries. This employs a general method for partitioning grain boundary orientation into specific sets of Shockley partial dislocations that produce the stacking fault arrays. To illustrate, we present HRTEM observations and atomistic calculations of (111)/(112) facets at 90 degree <110> boundaries in gold. This type of interface dissociates into a periodic array of stacking faults with one fault to every three close-packed planes, an arrangement that is equivalent to 9R stacking (abc/bca/cab). We compare our results with earlier observations of 9R stacking at $\Sigma=3$ (112) boundaries. Key geometrical features of the relaxations at both types of interface, including the distribution of stacking faults and the bending of planes near the boundaries, can be understood in terms of the dislocation structure of the interface. Both interfaces are composed of a periodic array of pure-edge (90 degree) and mixed (30 degree) character Shockley partial dislocations. In the $\Sigma=3$ interface, the ratio of 90 degree:30 degree dislocations is 1:2, whereas in the {111}/{112} interface the ratio is reversed, 2:1. In both cases, separation of these dislocations produces the 9R sequence by introducing a stacking fault every third plane. These results demonstrate the important role of Shockley partial dislocations as fundamental elements of interfacial structure in FCC metals.

This work is supported by the U.S. DOE, in part by the OBES-DMS, under contract DE-AC04-94-AL85000.

R5.2

THE INFLUENCE OF JUNCTION GEOMETRY ON GRAIN BOUNDARY STRUCTURE IN NANO-TWINNED <110> GOLD THIN FILMS. Gene Lucadamo and Douglas L. Medlin, Sandia National Laboratories, Thin Film and Interface Science Department, Livermore, CA.

Junctions are fundamentally related to dynamic processes, such as grain boundary migration and stress relaxation, that control microstructure evolution. We present results from the study of a four-fold junction containing a near- $\Sigma 81$ boundary in a <110> gold film. The junction related to the boundary was formed as a result of profuse nanotwinning in the as-deposited film. Multiple twinning creates a subset of well-characterized, high-angle boundaries of the

type $\Sigma 3^n$ ($n = 1,2,3$) and their associated intersections, which are important in applications of grain boundary engineering. A classic example is the $\Sigma 3$, $\Sigma 3$, $\Sigma 9$ tri-junction. A closely related configuration is the $\Sigma 3$, $\Sigma 3$, $\Sigma 9$, $\Sigma 81$ quad-junction observed here. In this case, we find that the $\Sigma 81$ boundary had dissociated. High-resolution transmission electron microscopy (HRTEM) revealed that the dissociation led to periodic sections of hcp stacking. A recent model that describes tilt boundaries as ordered arrays of partial dislocations was used to assist in the interpretation of the atomic structure. The results of this analysis accurately predict the arrangement of stacking faults and are consistent with the experimental results. Understanding the defect content and atomic structure of the boundary in regard to the junction crystallography then provides a means of addressing the mechanisms responsible for the dissociation.

This work is supported by the US Department of Energy, in part by the Office of Basic Energy Sciences, Division of Materials Sciences, through contract DE-AC04-94-AL85000.

R5.3

EFFECTS OF INTERFACE STRUCTURE ON GOLD FILM ADHESION. N.R. Moody, N. Yang, Sandia National Laboratories, Livermore, CA; D.P. Adams, Sandia National Laboratories, Albuquerque, NM; W.W. Gerberich, University of Minnesota, Minneapolis, MN.

Interfaces are important factors in determining properties and controlling reliability of thin film devices. They are critical factors in controlling the reliability of microcircuits with multilayer thin films and dissimilar material interconnects. These devices contain sub-micron-thin films with nanoscale structures and properties that vary markedly with changes in processing. However, the relationship between interface structure and properties is not well-defined. As a consequence, we have begun a study of this relationship in 200-nm-thick sputter deposited gold films using two substrate preparation procedures. High Resolution TEM shows these two procedures create dramatically different structures. One procedure creates 5-nm-thick epitaxial twins in the gold film along a well-defined film-substrate interface while the other creates a disordered interface and a gold film with random in-plane texture. Although the properties were similar, the interfacial fracture energies varied by a factor of three with the twinned microstructure exhibiting very low interfacial fracture resistance. When combined with fracture models, the results suggest that the epitaxial twins inhibit dislocation emission from interfacial cracks leading to low measured fracture energies.

This work supported by U.S. DOE Contract DE-AC04-94AL85000.

R5.4

DIRECT CHEMICAL STRUCTURE OBSERVATIONS OF $\Sigma 9$ GRAIN BOUNDARY ATOMIC STRUCTURE OF α -SiC BY HRTEM. Eriko Takuma and Hideki Ichinose, Univ of Tokyo, Dept of Materials Science, Tokyo, JAPAN.

Grain boundary chemical structure of a high purity α silicon carbide (6H-SiC) was investigated by an atomic resolution high voltage transmission electron microscope (ARHVTEM) viewing in <1120>. Owing to excellent resolution of this ARHVTEM at the Scherzer defocus condition, projected atomic potential image of a grain boundary was successfully obtained; Si atomic column appeared in darker contrast and C atomic column in thinner contrast. A (0001)/(1107) $\Sigma 9$ CSL grain boundary was observed between the base crystal and the third crystal, which was grown at the supplementary corner of 70.5degrees of the bicrystal. The tilt angle of this boundary was, therefore, fixed during the growth. One period of this boundary consisted of two 6-membered and four 5-membered and 7-membered rings. In the chemical structural point of view, this boundary consisted of three C-C pairs, one Si-Si pair and two non-paired Si. Two non-paired Si atoms may correspond to a coordination defect. Concluded chemical structure of this boundary was rather contradictory to the energy reduction rule found in the $\Sigma 3$ CSL boundary of 6H-SiC. However, flat and straight boundary trace of this boundary may claim reduced energy structure. Observed structure suggests that the grain boundary energy is adjustable by changing chemical structure under the fixed geometrical condition.

[1] E. Takuma and H. Ichinose, Philo. Mag. A, to be published.

R5.5

SLIP HARDENING AT INTERFACES IN NANOLAYERED COMPOSITES. C.H. Henager, Jr., R.J. Kurtz, H.L. Heinisch, Jr. and R.G. Hoagland, Pacific Northwest National Laboratory, Richland, WA.

When a glide dislocation passes through an interface between layers in coherent and semicoherent layered composites it creates a disconnection in the interface that becomes a source of stress due to several factors. The difference in the Burgers vector of the incoming and outgoing glide dislocation requires a residual dislocation at the interface. There is also a local relaxation in coherency stresses at the

interface due to the change in the interatomic interaction at the interfacial slip step. In addition, energy is required to create new interface at the slip step. The resulting disconnection thus interacts with subsequent trailing dislocations on the same and neighboring glide planes. In this paper, we present the results of an atomistic study in the layered, cube-on-cube Cu/Ni system that shows that a disconnection produced by slip acts as a potent slip barrier. The hardening increases with increasing step height and extends over a region of about two step heights on either side of the disconnection. This result explains some experimental observations on the uniformity of slip during rolling of nanolayered composites. We also examine the energy to create disconnections at interfaces in the Cu/Ni system, which may have implications for synthesis of layered composites. PNNL is operated by Battelle Memorial Institute for the U.S. Department of Energy and this work is supported by Basic Energy Sciences, DOE.

R5.6

ON THE ROLE OF MISFIT DISLOCATIONS AS OBSTACLES IN FCC/FCC NANOLAYERED COMPOSITES. Richard J. Kurtz, Richard G. Hoagland, and Charles H. Henager, Jr., Pacific Northwest National Laboratory, Richland, WA.

Explanations of the origins of strength in metallic nanolayered composites often invoke misfit dislocations. In epitaxial FCC/FCC systems, such as cube-on-cube Cu/Ni, very high strengths are achieved at thin layer thickness, e.g., less than 10 nm. In such systems, misfit dislocations are thought to act as obstacles to slip and peak strengths are reached when the misfit spacing begins to increase as the layer thickness becomes small. In this paper we present the results of an atomistic study of the strength of misfit dislocations as obstacles to glide in the cube-on-cube Cu/Ni system. In this system, a glide dislocation that cuts a misfit dislocation as it passes through the interface does not acquire a jog. However, it does produce a jog or jog/kink on the misfit depending on the Burgers vector of the glide dislocation. We find that the obstacle strength is relatively small, about 120 MPa increase in stress needed to cross the interface relative to a coherent interface free of misfit dislocations. Instead we find that, in an orthogonal array of misfit dislocations, those parallel to the glide planes exert much larger resistance than those that are cut. This research supported by the Materials Sciences Branch, Basic Energy Sciences, U.S. Department of Energy.

R5.7

IMPROVING INTERFACIAL QUALITIES OF METAL THIN FILMS: OXYGEN AS SURFACTANT. Hongmei Wen, Matthew Neurock, University of Virginia, Dept of Chemical Engineering, Charlottesville, VA.

The properties of thin films depend mainly on the atomic surface structures, especially the interfacial quality. A Cobalt-Copper system is a typical heterostructured system with problems of interfacial quality, like intermixing at the interface. Experiments find that a small amount of oxygen, acting as surfactant, can improve the interfacial quality of Co-Cu thin films. However, the mechanisms of oxygen functioning as surfactant are still unknown. In this work, the mechanisms are elucidated by the first principle calculations of Density Function Theory. When Cobalt thin film grows on Copper film, oxygen can selectively segregate Cobalt from Copper surface due to a stronger Co-O bond, about 0.7 eV stronger than Cu-O bond. Thus, interdiffusion happening on Co on Cu surface is reduced and the quality of Co-Cu thin films is improved. However, when Cu thin film grows on Co surface, the Oxygen doesn't segregate the Co to the surface owing to the trade-off among Co-Co, Cu-Co, Cu-Cu, Cu-O, and Co-O bonds, but the coverage of oxygen should not exceed 0.33 monolayer. During the thin film growth process, the oxygen can easily migrate to the top of surface once trapped inside of metal bulk with only 0.08 eV barriers from tetrahedral hole and around 0.4 eV barriers from octahedral hole to keep a clean Co-Cu thin film.

R5.8

INFLUENCE OF INTERFACES ON THE PHASE STABILITY IN NANOSTRUCTURED THIN FILM MULTILAYERS. G.B. Thompson, R. Banerjee, S.A. Dregia, H.L. Fraser, The Ohio State University, Department of MS&E, Columbus, OH.

Nanostructured thin film multilayers, comprising of alternating A/B layers, can exhibit metastable structures in one or both layers. From a classical thermodynamic viewpoint, the reduction in the interfacial energy is primarily responsible for this stabilizing effect. Based on this idea, a model has been constructed in which phase stability regions are represented as functions of both the bilayer thickness and the volume fraction of one of the layers. Applying this classical thermodynamic model to a single, previously reported hcp to bcc transformation in Zr for Zr/Nb multilayers, a phase stability diagram has been proposed. Various Zr/Nb multilayers, with different bilayer thicknesses and volume fractions, have been sputtered deposited. hcp

to bcc transformations in the Zr layer were confirmed by x-ray and electron diffraction. Furthermore the Zr/Nb stability diagram predicted a novel hcp Nb phase which was subsequently verified experimentally. Using Zr/Nb as a guide, a similar phase stability diagram was constructed and experimentally determined for Ti/Nb multilayers. For each multilayer system, the reduction in interfacial energy was calculated from the experimentally determined diagrams. These values were then compared to estimations of both the structural and chemical components of interfacial energy. The estimated structural component was based on the energy per unit area of a misfit dislocation network constructed using an O-lattice. A nearest neighbor bond model was used to approximate the chemical component. Good agreement was found between the experimental and calculated values. A detailed characterization of the Zr/Nb and Ti/Nb interfaces will be carried out using (high resolution) transmission electron microscopy, grazing incident x-ray diffraction, and atomic probe field ion microscopy. The results will be discussed in the context of phase stability in these multilayers.

R5.9

STRAIN ACCOMODATION MECHANISMS AT NANO-SCALE INTERFACES: A MOLECULAR DYNAMICS STUDY. M. Upmanyu, Computer Science and Mathematics Division, Oak Ridge National Laboratory; Materials Science Program, Colorado School of Mines and B. Radhakrishnan, Computer Science and Mathematics Division, Oak Ridge National Laboratory, Oak Ridge, TN.

We have performed molecular dynamics simulations of deformation of bicrystals in pure Al to study the mechanism of strain accommodation at nano-scale grain boundaries. The simulations are performed for an NPT ensemble using the well-known Parrinello-Rahman technique. Detailed analyses of the grain boundary structure before and after deformation (in the elastic as well as plastic regimes) are carried out to arrive at the atomistic mechanisms of strain accommodation. The spatio-temporal variation of excess grain boundary quantities such as grain boundary enthalpy, volume, etc., are investigated to ascertain the dependence of the strain accommodation mechanism on bi-crystallography. Finally, the effects of such strain accommodation mechanisms on nano-scale plasticity are discussed.

R5.10

HIGH STRENGTH NANOSCALE AL/AL₃Sc MULTILAYERS FORMED BY INTERFACE REACTION. Mark A. Phillips, Bruce M. Clemens, William D. Nix, Stanford University, Dept of Materials Science & Engineering, Stanford, CA.

Scandium additions to bulk aluminum alloys result in formation of Al₃Sc precipitates by homogenous nucleation. These precipitates are coherent with the matrix and produce a superior age-hardening effect. However, the maximum solid solubility of scandium in aluminum is about 0.25 at.%, so bulk systems contain only small interfacial regions. Thin film deposition processes allow deposition of layers of any range of compositions and any thickness. By construction of multilayer thin films with layer dimensions of a few nanometers, it is therefore possible to more closely examine interfacial properties and structure in this system. In these experiments, polycrystalline Al/Sc multilayer samples are grown via magnetron sputtering, enabling production of a significant volume of Al-Sc interfaces for study by thin film testing techniques. The ultimate goal is to determine the effect of barrier layers on the strength of Al films, but interesting microstructural information about the formation of interfaces is also obtained: The deposition of Sc on Al results in significant intermixing between the two components. Substrate curvature, measured *in-situ* during deposition, reveals behavior similar to that seen in other systems where a slow diffuser is deposited on a fast diffuser. The multilayer films (as-deposited and annealed) are characterized via High Resolution TEM, electron diffraction, analytical electron microscopy, and X-ray diffraction, revealing formation of a coherent crystalline Al₃Sc phase in the interfacial regions.

R5.11

A NOVEL NANOSTRUCTURED MEDIUM BY PLASMA TREATMENT FOR METAL REMOVAL FROM WATER VIA ION EXCHANGE. Donglu Shi, Wim van Ooij, Tony He, University of Cincinnati, Dept. of MS&E, Cincinnati, OH.

A plasma polymerization method has been developed to deposit an ultrathin functional film on the surfaces of nanoparticles. The modified surfaces of nanoparticles can serve many interesting functions for both fundamental research and industrial applications. In this presentation we will present a new nanostructure that can be used in ion exchange process for removal of metallic species from water. The core component in this novel ion exchange system is a matrix of nanoparticles consolidated in a porous fashion. Such a porous cluster consists of interconnected voids surrounded by a web of nanoparticles. On the surface of these nanoparticles, an extremely thin layer of polyacrylic film is coated by a plasma treatment. The polyacrylic film

will react with metallic ions in water. As a result of the high surface-to-volume ratio of these nanostructured clusters, the efficiency of ion exchange in the water flux is much higher than other types of traditional reactors. The experimental results will be presented from high resolution Transmission Electron Microscopy (HRTEM) and Time-of-Flight Secondary Ion Mass Spectroscopy (TOF-SIMS). The ion exchange mechanism via coated nanoparticles will be discussed.

R5.12

STUDY OF α -Al₂O₃ INTERDIFFUSION BARRIER IN Ba-FERRITE/SiO₂ THIN FILMS BY REAL TIME GLAZING INCIDENCE SYNCHROTRON X-RAY MEASUREMENTS.

Seok Joo Doh, Dept. of MS&E, POSTECH, Pohang, KOREA; Jung Ho Je, Dept. of MS&E, POSTECH, Pohang, Korea and Materials Science Division, Argonne National Laboratory, IL; Tae Sik Cho, Dept. of MS&E, Sangju National University, Sangju, KOREA.

Due to the large uniaxial anisotropy, excellent chemical stability, and high mechanical durability, BaFe₁₂O₁₉ (Ba-ferrite) thin film is an attractive candidate for future high-density magnetic recording and microwave circuit applications. The high crystallization temperature of Ba-ferrite film, however, limits the selection of commercial substrate materials such as thermally oxidized silicon (SiO₂) and glass. Especially, interdiffusion between Ba-ferrite film and SiO₂ substrate at high temperature deteriorates both interface (surface) roughness and magnetic properties of the film. In this article, we studied the interdiffusion phenomena and the role of α -Al₂O₃ buffer layer as an interdiffusion barrier in the Ba-ferrite/SiO₂ thin films by using real time glazing incidence synchrotron x-ray measurements, atomic force microscope, high resolution transmission electron microscope (HRTEM), and vibrating sample magnetometer. We first studied the interdiffusion phenomena in the interface of amorphous Ba-ferrite (1900-Å-thick)/SiO₂ film during real time annealing. The interdiffusion started to occur at \sim 700°C. As the annealing temperature increased up to 800°C, the interfacial reaction abruptly proceeded resulting in the high interface roughness and the deterioration of the magnetic properties. In order to control the interdiffusion at the high temperature, we introduced α -Al₂O₃ buffer layer (110-Å-thick) in the interface of Ba-ferrite (1900-Å-thick)/SiO₂ film. During the annealing of Ba-ferrite/ α -Al₂O₃/SiO₂ thin film even at \sim 800°C, the interface (surface) was very smooth, compared to that of the Ba-ferrite/SiO₂ thin film by the real time glazing incidence synchrotron x-ray measurements. The smooth interface of the film was also clearly shown by the cross-sectional HRTEM. The magnetic properties, such as saturation magnetization and intrinsic coercivity, were also enhanced, due to the inhibition of interdiffusion by the α -Al₂O₃ buffer layer. Our study suggests that the α -Al₂O₃ buffer layer act as a useful interdiffusion barrier in the Ba-ferrite/SiO₂ thin films for high-density recording media.

SESSION R6: POSTER SESSION
MAGNETIC MATERIALS
Tuesday Evening, April 2, 2002
8:00 PM
Salon 1-7 (Marriott)

R6.1

DEFECT- AND INTERFACE-INDUCED MAGNETIC PHASE

TRANSITIONS IN NANOSTRUCTURES. Igor Suzdalev, Vladimir Buravtsev, Yurii Maksimov, Sergey Novichikhin, Institute of Chemical Physics, RAS, Moscow, RUSSIA.

Intercluster interactions are the most important factor governing formation and properties of nanostructures and nanomaterials. These interactions are defined by the properties of surfaces and interfaces. For the testing of these properties depicted in terms of defect density, magnetic phase transitions in nanostructures can be used. The thermodynamic model of the first and second order magnetic phase transitions regulated by the optimal (maximum) of defect density at the some cluster sizes in nanostructures is developed. Two types of nanostructures were synthesized and studied: 1. obtained by solid state chemical reaction of iron salts and 2. obtained by high pressure with shear loaded metal europium mixed with α - γ iron oxide nanostructures. The first order magnetic phase transitions were obtained for α - γ iron oxide nanostructures. In these nanostructures the magnetization and magnetic ordering disappeared by the jump in the temperature range T=120-300K that much lower of the Neel and Curie points for second order (Langevine type) magnetic phase transitions in the corresponding bulk materials. On contrary, the nanostructures 2 showed only second order magnetic phase transitions with increased Neel point when compared with the corresponding value for bulk metal europium. These phenomena and characteristics are in agreement with predictions and estimations of thermodynamic theory of magnetic phase transitions in nanostructures induced by defect and interface interactions.

R6.2

CHARACTERIZATION OF COLOSSAL MAGNETORESISTIVE (CMR) THIN FILMS WITH AN X-RAY DIFFRACTION METHOD. M.F. Kupriyanov, Denis Korolkov, K.G. Abdulvahidov, Rostov State Univ, Rostov-on-Don, RUSSIAN FEDERATION.

When making thin films one should take into account changes of their structural and physical properties which depend on film thickness (nanodimensional effects). Modernization of an X-ray structure analysis has been made to allow for the influence of these changes on thin film diffraction pattern. The modernization consisted in considering the contribution of some parameters, such as: (i) atom parameters (positions, occupation, Debye-Waller factor) - in a unit cell scale; (ii) structural microinhomogeneities and regions of coherent scattering - in a crystalline block scale; (iii) textures and twin structures in polycrystalline thin films - in an object scale. The software was tested on CMR thin films, such as La_{1-x}CaxMnO₃.

R6.3

STUDY OF LIQUID INTERFACIAL FILMS IN NANOSTRUCTURED Nd₂Fe₁₄B BY MEANS OF TRACER DIFFUSION.

F. Ye, S. Herth, M. Eggersmann, Forschungszentrum Karlsruhe, Inst für Nanotechnologie, Karlsruhe, GERMANY; O. Gutfleisch, Inst für Festkörper- und Werkstofforschung Dresden, GERMANY; R. Würschum, Inst für Tech Physik, Tech Univ Graz, AUSTRIA.

Tracer diffusion has proven to be a powerful tool in the current topic to what extent interfaces of nanostructured materials differ from conventional grain boundaries[1]. In the present work tracer diffusion is applied to the study of intergranular melting of Nd-enriched grain boundaries in nanocrystalline Nd₂Fe₁₄B hard magnets. These studies aim at the understanding of the metallurgical processing of these materials and, in particular, at the assessment of how interfacial liquid films in nanostructured materials are affected by effects of confinement due to the adjacent liquid-crystal interfaces. The grain-boundary (GB) diffusion was measured below and above the intergranular melting transition (T \sim 675°C) using the radiotracer technique with the isotope ⁵⁹Fe. An evaluation of the diffusion profiles on the basis of grain-boundary diffusion kinetics of type B yields the product $D_{GB}\delta = 1.64 \times 10^{-9} \exp(-2.2eV/kT) \text{ m}^3 \text{ s}^{-1}$ of the grain boundary diffusivity D_{GB} and thickness δ in the solid phase assuming a volume self-diffusivity as in α -Fe. Above the intergranular melting transition a substantial increase of $D_{GB}\delta$ could be observed. The intergranular melting process is discussed in view of the fact that no abrupt increase of $D_{GB}\delta$ occurs.

[1] H. Tanimoto, P. Farber, R. Würschum, Valiev R. Z., and H. -E. Schaefer, "Self-Diffusion in High-Density Nanocrystalline Fe", Nanostr. Mater. 12 (1999) 681.

R6.4

CALCULATED ELECTRONIC CHARGE OF METALLIC MULTILAYERS FORMED BY NOBLE AND TRANSITION METALS. A.M. Mazzone and S. Milita, C.N.R.-Istituto LAMEL, Bologna, ITALY.

Thin metallic films constitute one of the key ingredients in the development of new storage devices characterized by high density and miniaturization and their practical interest has fueled intensive researches, both theoretical and experimental. Known properties of multilayers are quantum-well states, oscillatory magnetic coupling and conductivity. These properties are attributed to a 2D electronic structure, as in the isolated monolayer. In experiments, however, the pure 2D behavior may be perturbed by interactions with the supporting substrate and/or by inter-layer coupling. It is therefore important to assess which are the modifications of the electronic charge induced by the thickness. In this study full-potential linearized-augmented-plane-wave(FPLAPW) calculations are performed to investigate the properties of the electronic charge of metallic multilayers formed by non-magnetic and magnetic elements (i.e. Ag, Cu and Fe). The multilayer structure is either homogeneous, formed by n layers of the element A, or composition-modulated of the type (nA)(nB) or (AB)n. The calculations, carried out at paramagnetic level, illustrate the dependence of the density of states on the multilayer thickness and composition. The main feature of the electronic charge of the multilayers is the absence of charge intermixing and hybridization. For structures with a number of layers less than 5 the density of states bandwidth has a decrease, with respect to the bulk value, approximately proportional to the reduced coordination. At this critical thickness and above, a noticeable difference exists between the charge in the outer layers, with reduced coordination and bandwidth, and the central layers with a bulklike density of states. Averaging between these contributions leads to the re-installment of bulklike properties. These results are in agreement with quantum mechanical calculations carried out for similar systems and with experiments.

SESSION R7: NANOSTRUCTURED INTERFACES IN
STRUCTURAL AND MAGNETIC MATERIALS
Chairs: Juergen M. Plitzko and Kevin T. Moore
Wednesday Morning, April 3, 2002
Salon 5/6 (Marriott)

8:00 AM *R7.1

OBSERVATIONS OF SIZE- AND ORIENTATION-DEPENDENT BEHAVIOR AT INTERFACES IN METALS. U. Dahmen, T. Radetic, NCEM, LBNL Berkeley, CA; E. Johnson, Oersted Lab, Niels Bohr Institute, University of Copenhagen, GERMANY; F. Lanaon, CENG Grenoble, FRANCE.

The behavior of crystalline interfaces depends on crystal size, shape and orientation. This talk will present several examples for size-dependent behavior on the nanoscale observed directly by high resolution transmission electron microscopy. We have investigated Pb inclusions in Al, and high angle grain boundaries in Au. In-situ observations of small liquid Pb inclusions in Al show that nanosize inclusions have melting points and diffusion rates that increase with decreasing size. Solid Pb inclusions on grain boundaries in Al display compound shapes bounded by two different interfaces. A large difference is found in the melting behavior at the different interfaces on the same particle. This behavior also depends strongly on local curvature. Finally, we have observed that 90° tilt grain boundaries in Au can undergo a new type of dissociation at their line of intersection with the free surface. These observations correlate well with molecular dynamics calculations. The examples shown in this work can be understood as a result of the increased importance of interface structure in the nanoscale size regime.

This work is supported by the Director, Office of Science, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-ACO3-76SF00098.

8:30 AM R7.2

ATOMIC STRUCTURE OF [110] TILT GRAIN BOUNDARIES IN FCC METALS. K.L. Merkle and L.J. Thompson, Materials Science Division, Argonne National Laboratory, Argonne, IL.

The structure of grain boundaries (GBs) in fcc metals strongly depends on macroscopic geometric parameters but may also be sensitive to details of inter-atomic interactions. To investigate the effect of different inter-atomic potentials we study GB structures in Al and Au by high-resolution transmission electron microscopy (HREM). High-angle [110] tilt GBs in particular are suited for such a study, since in many instances relaxation modes involve the introduction of stacking disorder. Al and Au serve as model materials with high and low stacking fault energies respectively. Nano-structured bicrystalline films were manufactured by an epitaxial templating technique. The films were grown with boundaries of the desired in-plane [110] misorientation. In this manner island grains of nano-scale dimensions were often formed that could be used to study interface structures as a function of GB inclination. When comparing Al and Au films of identical GB misorientation differences in faceting behavior as well as the atomic-scale GB structures could be investigated. The Al GB structures in some cases were strikingly different from Au GBs, notably compared to the stacking-fault type dissociations of high-angle GBs in Au, as for example in the $\langle \text{sum} \rangle = 41$ and $\langle \text{sum} \rangle = 33$ GBs. The results will be discussed in terms of GB models based on embedded atom calculations.

This work was supported by the U. S. Department of Energy under contract No. W-31-109-ENG-38.

8:45 AM R7.3

IN-SITU STUDIES OF GRAIN BOUNDARY MIGRATION. K.L. Merkle and L.J. Thompson, Materials Science Division, Argonne National Laboratory, Argonne, IL; F. Philipp, Max-Planck-Institut für Metallforschung, GERMANY.

Properties and processing of polycrystalline materials often critically depend on what happens during thermally activated migration and possible restructuring of grain boundaries, but very little is known concerning the atomic-scale mechanisms involved. Here we use in-situ high-resolution transmission electron microscopy to study grain boundary motion at elevated temperature. High-purity thin film samples of Au and Al containing nanograins with a predetermined misorientation were prepared by epitaxial templating. The direct atomic-scale observations of grain boundaries at elevated temperature allows identification of migration modes for different misorientations and as a function of the grain boundary inclination. Depending on geometry, grain boundary migration has been observed to involve widely different processes, including glide, climb, and collective effects, involving small groups of atoms. We will discuss our observations in view of previously proposed mechanisms, macroscopic observations, and recent atomistic simulations.

9:00 AM R7.4

ATOMIC SCALE PROCESSES IN NANOCRYSTALLINE METALS: A MOLECULAR DYNAMICS INVESTIGATION. A. Hasnaoui, P.M. Derlet, H. Van Swyghoven, Paul Scherrer Institut, Villigen PSI, SWITZERLAND.

The use of large-scale molecular dynamics in the study of structural and mechanical properties of nanocrystalline (nc) fcc metals, provides a level of atomic detail that still remains inaccessible to experiment. In the present work we attempt to classify a number of atomic processes taking place in the confined grain boundaries during annealing and under applied stresses. Detailed examples of occurring mechanisms such as correlated and uncorrelated atomic shuffling, stress-assisted diffusion and thermal diffusion are given (Van Swyghoven and Derlet, Phys. Rev. B (in press) 2001). The accommodation mechanisms, such as grain boundary and triple junction migration are discussed. It is demonstrated that all mechanisms tend to increase the order and decrease the energy in the nanosized grain boundary. By calculating the TEM image of the simulated sample direct comparison of the structure of the grain boundaries with experimental observation is made possible.

9:15 AM R7.5

MOLECULAR DYNAMICS STUDY OF MASS TRANSPORT IN NANOCRYSTALLINE COPPER. P. Geyssmans, Y. Champion, M.J. Hytch, C. Langlois and V. Pontikis, Centre d'Etudes de Chimie Métallurgique, CNRS UPR A2801, Vitry-sur-Seine Cedex, FRANCE.

Surface and bulk self-diffusion have been studied in nanocrystalline copper by using Molecular Dynamics in the canonical ensemble and an adapted n-body, phenomenological potential. The model nanocrystal has been grown from the liquid in which several crystalline seeds had been adequately introduced prior to cooling. Our computations show that surface and bulk atomic mean square displacements in the nanocrystal, are enhanced with respect to those computed for the single-crystalline material. Moreover, we found that diffusion is predominantly mediated by vacancies although a non-negligible contribution to the macroscopic mass transport at the surface may originate from adatom mobility. The above findings are discussed and compared with computational and experimental data. Actually, mean activation energy for grain-boundaries diffusion, measured from sintering experiments (and confirmed by other techniques) is extremely low (about 50kJ.mol⁻¹) compared to grain-boundary diffusion in microcrystalline copper (107 kJ.mol⁻¹).

9:30 AM R7.6

MANIPULATIONS OF NANOPARTICLE CHAIN AGGREGATES IN TRANSMISSION ELECTRON MICROSCOPY. Yong J. Suh, Sheldon K. Friedlander, University of California, Dept of Chemical Engineering, Los Angeles, CA; Sergey V. Prikhodko, University of California, Dept of Materials Science and Engineering, Los Angeles, CA.

Experimental difficulties in studying nanostructures stem from their small size, which limits the use of traditional techniques for measuring their physical properties. We have developed a nanostructure manipulation device to apply tension to nanoparticle chain aggregates (NCAs) mounted in a transmission electron microscope. A 1 mm long slit was cut in the center of a lead alloy disc, measuring 3 mm in diameter and 0.2 mm in thickness. The disc was heated to about 140°C before it was pressed between two quartz slides. The disc was then thinned by mechanical dimpling and ion milling until holes developed around the slit. The edges of the slit were 0.2 to 3 μm in thickness while the gap between them was up to a few microns. This disc was bonded to the two plates of a cartridge. The slit could be widened or narrowed at controlled speeds of 0.5 to 300 nm/s by means of a commercially available specimen holder to which the cartridge was attached. The system was tested using titania chain aggregates deposited across the slit. The ends of the NCA remained attached to the edges of the slit which was widened at about 0.7 nm/s. In this way, the NCA was stretched up to 176% of its initial length before breaking toward the middle of the chain. The NCA contracted rapidly after breaking, showing its elastic behavior. By minimizing the beam exposure, this device makes it possible to study chain aggregates made of materials susceptible to degradation under the electron beam; we are currently studying the effect of tension on morphology of carbon NCAs, which are of interest in air pollution (e.g., diesel emissions) and as reinforcing fillers in the manufacture of rubber.

9:45 AM R7.7

INFLUENCE OF ULTRA-FINE PARTICLES ON NANO-CRYSTALLINE Ni COATINGS. Jianhong He, Julie M. Schoenung, Enrique J. Lavernia, Univ. of California, Irvine, School of Engineering, Irvine, CA.

Nanocrystalline Ni powders and thermally sprayed coatings, containing ultra-fine AlN particles were synthesized and characterized. The results indicated that the presence of AlN particles in the powders drastically decreased the dimension of agglomerates formed by cryomilling and increased surface roughness of the agglomerates. The AlN phase was broken down into ultra-fine particles of approximately 30 nm. These particles were dispersively embedded into the Ni matrix and enhanced the development of a nanocrystalline structure in the Ni matrix during cryomilling. Selected area diffraction pattern with transmission electron microscopy and X-ray mapping with scanning electron microscopy confirmed the presence of AlN particles in the coatings. The presence of AlN particles also led to an increase in the amount of NiO phase that was distributed in the coating, and seen in the form of ultra-fine, round particles. AlN particles increased the microhardness of the Ni coating by approximately 60%. Indentation fracture results also indicated the fine, dispersed AlN particles raised apparent toughness of the Ni coating. The synthesized Ni coatings containing ultra-fine AlN particles were characterized as equiaxed nanocrystalline grains with an average size of 24 nm in which twins were observed. The increase in microhardness resulted from both grain refinement and the presence of ultra-fine particles. However, the latter played the primary role in strengthening.

10:30 AM R7.8

GRAIN BOUNDARY DEFECTS AND METASTABILITY EFFECTS IN NANOSTRUCTURED SPD-ALLOYS. Ruslan Z. Valiev, Ufa State Aviation Technical University, Institute of Physics of Advanced Materials, Ufa, RUSSIA.

Presently it is well established that severe plastic deformation (SPD), i.e. intense plastic straining under high imposed pressure can essentially refine microstructure till a nanometer range and this provides a potential to achieve their new and extraordinary properties [1,2]. However, the SPD-processed metals have usually complex nanostructures characterized by not only very small grain sizes, but also specific grain boundaries, containing very high density of dislocations and disclinations. This paper focuses on recent studies of grain boundaries structure and their relationship with unique properties in SPD-fabricated materials, namely, in several Al- and Fe-alloys and intermetallics. It has been shown that these materials are characterized by formation of non-equilibrium grain boundaries with high excess energy and long-range stresses. The nature of such non-equilibrium grain boundaries has been studied by TEM/HREM, X-ray and DSC, and their important role in metastability of these SPD-alloys associated with formation of supersaturated solid solutions or amorphization of intermetallics phases is established. During further heating of these bulk metastable nanostructured alloys the ageing effects take place and the processed alloys demonstrate unique and extraordinary mechanical (very high strength and ductility, superplasticity) and magnetic hysteric properties. Origin of these enhanced properties related with non-equilibrium grain boundaries and their recovery is considered and discussed.

10:45 AM R7.9

STRUCTURE, PHASE TRANSFORMATION AND TWINNING OF MAGNETIC FePt NANOCRYSTALS. Z.L. Wang*, Z.R. Dai* and Shouheng Sun#. *School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA. #IBM T.J. Watson Research Center, Yorktown Heights, NY.

Depending on the Fe to Pt elemental ratio, the Fe-Pt alloys can display chemically disordered face centered cubic phase or chemically ordered phases. We report detailed microscopic studies on phase transformation, coalescence and twin structure formation of thermally annealed 6 nm FePt nanocrystals under high vacuum on an amorphous carbon surface. Our high-resolution transmission electron microscopy (HRTEM) studies show that A1 to L10 phase transformation occurs at 530°C. The multilayered nanocrystal assemblies coalesce to form larger grains at 600°C. Shape and surface atomic arrangement of the monodisperse FePt magnetic nanocrystals and their evolution induced by annealing have been studied. Truncated octahedron enclosed by flat {100}, stepped {111} and zig-zag {110} facets is the dominant shape adopted by the as-synthesized FePt nanocrystals. The Marks decahedron shaped FePt nanocrystals and icosahedron related multiply twinned FePt nanocrystals are also identified in the as-synthesized nanocrystals. A new structural model the multiply twinned nanocrystals related to icosahedron has been proposed. After annealing, the {110} facet disappears; the regular cuboctahedron becomes a dominant shape for the chemically ordered FePt nanocrystals. Atomic arrangement of the FePt nanocrystals surfaces is the same as that in the volume although some defects such as atomic steps and kinks exist. Iron atoms are preferably the terminating layer of the {100} surface after annealing.

11:00 AM R7.10

PROBING BURIED INTERFACES WITH SOFT X-RAY

STANDING WAVES. S.-H. Yang, Materials Sciences Division, Lawrence Berkeley Laboratory, Berkeley, CA; B.S. Mun, N. Mannella, L. Zhao, C.S. Fadley, Materials Sciences Division, Lawrence Berkeley Laboratory, Berkeley, CA; Department of Physics, University of California at Davis, Davis, CA; S.-K. Kim, Department of Physics and the Center for Nanospinics of Spintronic Materials, Korea Advanced Institute of Science and Technology, Taejon, KOREA; J.B. Kortright, J. Underwood, Materials Sciences Division, Lawrence Berkeley Laboratory, Berkeley, CA; E. Arenholz, A. Young, Z. Hussain; Advanced Light Source, Lawrence Berkeley Laboratory, Berkeley, CA.

We report a novel type of non-destructive method for spectroscopically probing buried nanometer-scale interfaces and other nanostructures with soft x-ray standing waves. Strong standing waves with a period of 4.0 nm and an approximately 4 contrast ratio are created above a synthetic multilayer of form $[B_4C/W]_{40}$. By growing a wedge-shaped Fe/Cr bilayer on top of this multilayer, the mechanical translation of a focussed synchrotron radiation beam across the sample is converted into a translation of the standing wave through the interface. Analyzing various core photoelectron intensities as a function of angle and beam position permits deriving layer thicknesses and interface mixing/roughness scales. Magnetic circular dichroism in photoemission from the 2p and 3p levels of Fe and Cr further permits deriving the positions and widths of regions with decreased (increased) ferromagnetic alignment for Fe (Cr), showing that Cr is antiferromagnetically aligned with respect to Fe just below the center of the interface, and that the equal-concentration region in the center of the interface strongly inhibits magnetic alignment for both species. The magnetically-altered regions are only 1-2 atomic layers in thickness. 3s spectra from Fe and Cr spectra also indicate that the local spin moments on both atoms do not change on crossing the interface. This method should have a range of applications for the characterization of nanostructures and their interfaces.

11:15 AM R7.11

A MOLECULAR DYNAMICS INVESTIGATION OF THE VIBRATIONAL PROPERTIES OF NANOCRYSTALLINE Ni. P.M. Derlet, H. Van Swygenhoven, and U. Stuhr, Paul Scherrer Institute, Villigen, SWITZERLAND.

Experimentally it is known that the vibrational density of states (VDOS) of nanocrystalline material exhibit enhanced low and high frequency modes, when compared to the polycrystalline regime. In the present work the VDOS of model bulk nanocrystalline (nc) Ni samples is calculated for samples with average grain diameters ranging between 5nm and 12nm. An enhancement of the density of states at both low and high phonon frequencies is observed. By determining the component of the vibrational density of states arising from the grain and grain boundary atoms, it is shown that the anomalous features seen in the nc material VDOS come predominantly from the interfacial vibrational modes. It is found that the low frequency enhancement exhibits a non-integer power law behavior that might suggest a reduced dimensionality for the GB vibrational modes (Derlet, et al, Phys. Rev. Lett, **87** 205501-1 (2001)).

11:30 AM R7.12

ATOMIC LEVEL CHARACTERIZATION OF NICKEL CRYSTALLITES OF NANOMETER DIMENSION. D. Kumar, Center for Advanced Materials and Smart Structures, North Carolina A&T State University, Greensboro, NC; H. Zhou, J. Narayan, G. Duscher, A.V. Kvit, Department of MS&E, NC State University, Raleigh, NC; Andrew Lupini, S.J. Pennycook, Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN; J. Sankar, Center for Advanced Materials and Smart Structures, North Carolina A&T State University, Greensboro, NC.

Understanding the atomic structures and chemistry of nanoparticles and particle-host matrix interfaces is often critical to structure-property relationship in solid state structures of nanoscale dimension. In this paper we present our results from investigations in which scanning transmission electron microscopy with atomic number contrast (STEM-Z) and energy loss spectroscopy (EELS) were used to understand the atomic structure of Ni nanoparticles and interface between the nanoparticles and the surrounding matrices. Since Z-contrast imaging and EELS could be performed simultaneously, we were able to make direct correlations between structure and chemistry of the Ni nanoparticles which were embedded in amorphous alumina and crystalline TiN matrices using a pulsed-laser deposition process. It was interesting to learn from EELS measurements at individual grains and interface planes that Ni in alumina matrix does not form an ionic bond at the interface indicating the absence of metal-oxygen bond at interface. The absence of metal-oxygen bond, in turn, suggests the absence of any dead layer on Ni nanoparticles even in an oxide matrix.

11:45 AM R7.13

INVESTIGATION OF SURFACE SEGREGATION IN NIPT ALLOY

THIN FILM ON ATOMIC SCALE. Honghui Zhou, Alexander Kvit, Gerd Duscher, Jagdish Narayan, NSF Center for advanced Materials and Smart Structures, Department of Materials Science and Engineering, North Carolina State University, Raleigh, NC.

NiPt alloy system has been a subject of intensive research for many years because of its extraordinary magnetic properties as well as its unique orientation-dependent surface segregation property. In this study, NiPt alloy thin films were grown by pulsed laser deposition (PLD) technique. The surface segregation was studied by both high-resolution transmission electron microscopy (HRTEM) and scanning transmission electron microscopy (STEM). The element-mapping obtained by simultaneously performing Z-contrast imaging and electron energy loss spectroscopy (EELS) made it possible to visualize and understand the atomic structure and chemistry of the interface of segregation. The results were compared with that of the theoretical studies.

SESSION R8: NANOSTRUCTURED INTERFACES IN OXIDES AND ELECTRO-OPTICAL MATERIALS

Chair: J. R. Jinschek
Wednesday Afternoon, April 3, 2002
Salon 5/6 (Marriott)

1:30 PM R8.1

PHOTOLUMINESCENCE OF NANO-SCALED YAG: Ce,Sm,Cr PHOSPHOR POWDERS. In-Gann Chen¹, Yulin Chen¹, Chii-Shyang Hwang¹, F.S. Juang², S.J. Chang³, and Y.K. Su³. ¹Department of MS&E, National Cheng Kung University, Tainan, TAIWAN. ²Department of Electro-Optics Engineering, National Huwei Inst. of Tech, Huwei, Yunlin, TAIWAN. ³Department of Electrical Engr, National Cheng Kung University, Tainan, TAIWAN.

Four series of YAG:Ce phosphor powders were synthesized by solid state, co-precipitation, and sol-gel (with two different growth inhibitors) methods, which results in the average particle sizes of 800, 56, 43, and 32 nm respectively. All the nano-scale YAG powders were heat treated below 1000 C. Both TEM and XRD results of these nano-scale YAG powders show high degree of crystalline structure. Photoluminescence (PL) characterization shown that the nano-scale YAG phosphor powders show a higher intensity of luminescence than that of sub-micro sized sample. The effect of different Ce doping level on the PL of (Y_{3-x}Ce_x)Al₅O₁₂ shows a maximum at x ~ 0.01. The effect of Y substitution by Gd and La on the PL properties was investigated. The CIE chromaticity coordinates were determined to show different trends of shift in PL spectra. Systematic study of the processing parameters characterized by DTA/TGA, XRD, FTIR, and BET will be discussed in detail in the report.

1:45 PM R8.2

THE ELECTRONIC STRUCTURE OF DIAMOND NANOPARTICLE STUDIED BY X-RAY ABSORPTION AND ELECTRON ENERGY LOSS SPECTROSCOPY. T. van Buuren, J. Piltzko, C.F.O. Bostedt, N. Franco, L.J. Terminello, Lawrence Livermore National Laboratory, Dept. of Chemistry and Material Science, Livermore, CA.

The conduction band edge of bulk diamond and diamond nanoparticles were measured using x-ray absorption and high-resolution transmission electron microscopy electron energy loss spectroscopy (HRTEM/EELS). The diamond nanoparticles are commercially available products from the Straus chemical corporation and are synthesized in a denotation wave from high explosive material. X-ray diffraction and TEM show that the diamond nanoparticles are crystalline and approximately 3.5 +/- 1.0 nm in diameter. The nanodiamond K-edge absorption show the same spectra features as the bulk diamond with low impurity levels. The C1s core exciton feature clearly observed in the bulk diamond is not observed in the nanodiamond spectra. A possible explanation for this effect is due to decrease in lifetime due to quantum confinement effects on the core exciton. The depth of the second gap in the nanodiamond spectra is shallower than that of bulk diamond. This effect has been observed previously and has also been attributed to quantum confinement. The conduction band edge of the nanodiamond particles is not blue shifted with respect to the bulk diamond edge contrary to a recent publication that has reported large conduction band shifts in CVD grown diamond nanoclusters. To resolve this difference experiments are in progress to measure the nanodiamond conduction band edge from the EELS spectra acquired with a field emission TEM. We compare the conduction band edge measured by x-ray absorption with the EELS spectra measured on individual nanoparticles and comment on the difference. The electronic structure of the nanodiamond will be compared to recent results on Si and Ge nanoclusters and the effects of reduced sizes on the band edges of the group IV semiconductor will be discussed.

This work is supported by the US-DOE, BES Material Sciences under contract W-7405-ENG-48, LLNL. Y.K. Chang et.al. PRL 82, 5377 (1999).

2:00 PM R8.3

GROWTH OF GaN NANORODS ON (0001) SAPPHIRE SUBSTRATES BY HYDRIDE VAPOR PHASE EPITAXY. Hwa Mok Kim, Doo Soo Kim, Young Wook Chang, Deuk Young Kim, Tae Won Kang, Dongguk Univ, Quantum-Functional Semiconductor Research Center, Seoul, KOREA.

GaN nanorods were grown on (0001) sapphire substrates by hydride vapor phase epitaxy (HVPE) through a self-assemble process. The nanorods were grown at high growth rate, with the c-axis maintained perpendicular to the substrate surface. The dependence of rod diameter and density on growth conditions was systematically investigated. The average diameter was minimized to 50 nm and the density of the GaN nanorods was 100×10^{10} rods/m². Cathodoluminescence was used for studying the luminescence properties of nanorods.

2:15 PM R8.4

CHARACTERIZATION OF GaN/AlN QUANTUM DOT MULTILAYERS USING X-RAY GRAZING INCIDENCE TECHNIQUES. V. Chamard¹, T.H. Metzger¹, E. Bellet-Amalric², B. Daudin², H. Mariette², C. Adelmann², G. Mula^{2,3}. ¹European Synchrotron Radiation Facility, Grenoble Cedex, FRANCE. ²CEA-CNRS, Département de Recherche Fondamentale sur la Matière Condensée, CEA/Grenoble, Grenoble Cedex, FRANCE. ³Also at INFN and Dipartimento di Fisica, Cittadella Universitaria, Moserrato, Cagliari, ITALY.

The current interest in self-organized growth of strained semiconductor nano-structures is based on the possibility to achieve novel optical and electronic properties. Among them, nitride compounds are especially interesting due to their application in the blue-ultraviolet wavelength range. Using the Stranski-Krastanow growth mode, GaN truncated pyramidal shaped quantum dots (QDs) embedded in an AlN matrix are grown either in the wurtzite or in the zinc-blende phase. Due to the absence of internal electric fields, the zinc-blende phase is more interesting for optical applications, while the wurtzite QDs present better structural properties i.e. less dislocations and better size homogeneity. For application purposes, GaN QDs are typically embedded in an AlN matrix and stacked in multilayers. The resulting structure is investigated by x-ray grazing incidence techniques. The techniques are non-destructive, they provide depth resolution and average over a large ensemble of QDs. Shape, strain and ordering of the GaN QDs is obtained. Applying grazing incidence small angle x-ray scattering, we have quantified the strong vertical alignment of the dots as a function of the spacer layer thickness. With grazing incidence diffraction, the strain state of the dots and the matrix in the multilayer is analyzed. The variation of the QD size and lattice parameter has been investigated as a function of depth for a series of samples in the wurtzite phase.

3:00 PM R8.5

NANOSCALE POTENTIAL VARIATION OF GRAIN BOUNDARIES MEASURED BY OFF-AXIS ELECTRON HOLOGRAPHY. M.A. Schofield and Y. Zhu, Brookhaven National Laboratory, Materials Science Department, Long Island, NY.

Grain boundaries in polycrystalline materials strongly affect the transport properties of the material. In the case of the high-T_c superconductor Bi₂Sr₂CaCu₂O₈ (Bi-2212), (001) twist boundaries are dominant in c-axis aligned tapes and wires where, curiously, the superconducting critical current seems independent of twist angle. Furthermore, local phases consisting of additional or missing Cu-Ca-O planes are commonly observed at these twist boundaries. We have used off-axis electron holography to measure the potential and charge distribution across (001) twist boundaries in Bi-2212 in order to characterize the electronic structure at these interfaces. Many pure-phase twist boundaries were studied as well as several interfaces containing extra and/or missing Cu-Ca-O planes. We have found no correlation between the angle of grain-boundary misorientation and measured potential. For pure-phase boundaries the width of the interface potential is 5-10 Å or less, while for interfaces with extra or missing Cu-Ca-O planes, the observed grain-boundary potential is similarly narrow but shifted off the interface position indicating significant charge transfer. We have measured potentials ranging in magnitude from about 0.7 to 4.3 V relative to the mean inner potential of Bi-2212. From the measured grain-boundary potential we calculated the charge density across the interfaces, which we modeled as a sum of bound and free components of charge at the interface. For this model we obtain highly localized elastic strain fields and an average net lattice expansion of 0.3 Å at the interface. Nanoscale potential measurements of grain boundaries in SrTiO₃ and Ca-doped YBaCu₃O₇ will also be presented.

3:15 PM R8.6

THEORETICAL INVESTIGATION OF IMPURITIES AND VACANCIES AT NANOSTRUCTURED PEROVSKITE GRAIN BOUNDARIES. S. Gemming, M. Schreiber, Institut für Physik, Technische Universität, Chemnitz, GERMANY.

The influence of impurities and vacancies on the geometric and electronic structure of perovskite grain boundaries has been investigated with first-principles density-functional calculations, using the plane-wave band-structure code ABINIT [1] with ultrasoft pseudopotentials. The pure, undisturbed $\Sigma 3(111)[110]$ grain boundary in SrTiO_3 had been shown as a low-energy, rather bulk-like planar defect with a distinct nanostructure in earlier calculations [2]. In the present investigation oxygen vacancies and iron impurities are introduced both at the grain boundary and in its near vicinity. There is a thermodynamic driving force for the O vacancies to segregate to the grain boundary plane and form a trigonal superstructure. In contrast to the pure boundary, there is no expansion perpendicular to the grain boundary plane. One explanation might be that the lack of every third O ion leads to the contraction at the grain boundary. On the other hand, due to the lower O content in the boundary plane the adjacent Ti columns are formally reduced from Ti^{4+} to Ti^{3+} , and the Coulomb repulsion at the interface is diminished. The latter explanation is corroborated by Fe substitution of the Ti ions in the layer adjacent to a dense-packed boundary plane without O vacancies. Fe prefers a formal oxidation state of Fe^{3+} and acts as a model of Ti^{3+} . Also in this case no grain boundary expansion is observed, thus the Coulomb interactions between closely spaced columns dominate the precise geometric structure.

[1] The ABINIT code is a common project of the Université Catholique de Louvain, Corning Incorporated, and other contributors (URL <http://www.pcpm.ucl.ac.be/abinit>).
[2] S. Hutt, S. Köstlmeier, C. Elsässer, *J. Phys.: Condens. Matter* 13 (2001) 3949.

3:30 PM R8.7

NANO-SCALE RE123/RE211 INTERFACES ON THE SUPERCONDUCTIVITY IN THE RE-Ba-Cu-O MATERIALS. Shih-Yun Chen*, In-Gann Chen*, Chuan-Pu Liu*, Ping Chi Hsieh*, and M.K. Wu**. *Department of MS&E, National Cheng Kung University, Tainan, TAIWAN. **Department of Physics, National Tsing-Hwa University, Hin-Chu, TAIWAN.

Critical current density $J_c(H,T)$, of (RE)-Ba-Cu-O samples, where RE=Sm, Nd, and Y, with different $\text{RE}_2\text{BaCuO}_5$ (RE211) particles size distribution from μm to nm are measured. The TEM is used to observe the distribution of dislocations around the RE211 particles. The distribution of the defects at the interface between the nano-scaled RE211 particles and RE123 matrix are investigated. It is found that the density of dislocation is varying with the different curvatures of the RE211 particles. There is a higher density of dislocations around the small size RE211 particles especially with a sharp corner. These dislocations may act as pinning centers and thus enhance the J_c values of the superconductors. In addition, the total numbers of the nano-scaled RE211 particles can be increased with the addition of nm -size RE211 particles. Therefore, J_c property can be further enhanced due to the increase the number of effective pinning centers. A model to describe the relationship between J_c property and RE211 particle morphology will be discussed.
Supported by the NSC-90-2112-M-006-024

3:45 PM R8.8

THE LOCAL ELECTRONIC STRUCTURE AT HETERO-INTERFACES AND GRAIN BOUNDARIES IN ZnO THIN FILMS GROWN BY LASER DEPOSITION. Alexander Kvit, Gerd Duscher, Chunming Jin and Jagdish Narayan, NSF Center for Advanced Materials and Smart Structures, Department of Materials Science and Engineering, NCSU, Raleigh, NC.

The structure and chemistry of interfaces are known to affect the optical and electrical properties of wide-band gap semiconductor structures. High-quality $\text{ZnO}/\text{Si}(111)$ and $\text{ZnO}/\text{AlN}/\text{Si}(100)$ heterostructures grown by laser deposition were studied by conventional and high-resolution transmission electron microscopy (HRTEM). The local electronic structure was investigated by high resolution Z-contrast imaging using scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy in a scanning mode. Z-contrast imaging and EELS were performed simultaneously; so direct correlations between interface chemistry and local structure made. ZnO grain boundaries are composed of a periodic array of a basic structural unit. Based on the Z-contrast images a structural model of ZnO/AlN and ZnO/Si interfaces and ZnO grain boundaries was developed.

4:00 PM R8.9

ALIOVALENT DOPANT PROFILE IN NANOCRYSTALLINE TIN

DIOXIDE THIN FILMS AND ITS EFFECT ON ELECTRICAL PROPERTIES. Juan Dominguez, Haiping Sun and Xiaoping Pan, The University of Michigan, Dept. of Materials Science, Ann Arbor, MI.

Tin dioxide thin films are important electroceramics found in gas sensors, solar cells and transparent electrodes. The electrical properties of the material are determined by extrinsic defects such as oxygen vacancies and impurities. Doping with aliovalent elements can change the oxygen vacancy concentration and electrical properties of the films. In this work we investigate the distribution of dopants in films with several different microstructures. Both single crystal and nanocrystalline (textured and randomly oriented) films doped with different elements of varying ionic radius and valence were deposited using femtosecond pulsed laser ablation. The spatial distribution of the elements was determined using x-ray energy dispersive spectrometry (EDS) in a transmission electron microscope (2010F JEOL). The experimental results were compared to theoretical models based on space charge and elastic strain effects. Electrical property measurements confirmed the spatial variation with ionic radius and valence of dopants in tin dioxide films.

SESSION R9: POSTER SESSION
ELECTRO-OPTICAL MATERIALS
Wednesday Evening, April 3, 2002
8:00 PM
Salon 1-7 (Marriott)

R9.1

HRTEM EXIT WAVE RECONSTRUCTIONS FOR STRUCTURAL ANALYSIS OF ZIRCONIA AND TITANIA NANOCRYSTALS. Jane Bertone, Vicki Colvin, Rice Univ, Dept of Chemistry, Houston, TX.

In this investigation, chemically synthesized oxide nanocrystals with diameters on the order of 10 nm were studied using high-resolution electron microscopy (HREM) and exit wave reconstruction. Object exit wave functions of titania and zirconia nanocrystals were retrieved using Philips/Brite-Euram software for focal-series reconstruction. The atomic positions across particles were investigated and compared to simulated exit wave functions. Images of particles were segmented into different regions. These segments were then simulated separately in an attempt to more accurately report the true position of the object exit plane. In this way, more detailed information concerning surface features of nanoparticles is available.

R9.2

TOWARD RATIONAL DESIGN OF FAST ION CONDUCTORS: MOLECULAR DYNAMICS MODELING OF INTERFACES OF NANO-SCALE PLANAR HETEROSTRUCTURES. Jian-jie Liang, Paul W.-C. Kung, Accelrys Inc., San Diego, CA.

Increased ionic conductivity at nano-scale planar interfaces of CaF_2 — BaF_2 system was successfully modeled using molecular dynamics (MD) simulations. A criterion was established to construct simulation cells possessing any arbitrarily lattice mismatched interfaces while permitting periodic boundary condition. The experimentally observed ionic conductivity¹ at the 111 (CaF_2) — 111 (BaF_2) interface was reproduced. Even higher conductivity, by a factor of 7.6 relative to that at the 111 (CaF_2) — 111 (BaF_2) interface, was predicted for the 001 (CaF_2) — 001 (BaF_2) interface. Crystalline nanocomposites of the CaF_2 / BaF_2 system, where the [001] morphology is encouraged and with crystallite dimensions of about 4 nm, was proposed to give ionic conductivity approaching that predicted for the 001 (CaF_2) — 001 (BaF_2) interface.

1. N. Sata, K. Eberman, K. Eberl, J. Maier, *Nature*, 408, 946 (2000).

R9.3

INDIUM-INDIUM PAIR CORRELATIONS WITHIN THE WETTING LAYERS OF BURIED InAs/GaAs QUANTUM DOTS. B. Shin, B. Lita, and R.S. Goldman*, Univ of Michigan, Dept of Materials Science and Engineering, Ann Arbor, MI ; J.D. Phillips and P.K. Bhattacharya, Univ of Michigan, Dept of Electrical Engineering and Computer Science, Ann Arbor, MI.

Recently, arrays of stacked quantum dots have shown significant promise for a variety of novel device applications. In the InAs/GaAs system, the regions between the InAs islands, often termed the "wetting layers", contain a few layers of sparsely populated In atoms within a GaAs matrix. Recently, we used the wetting layers of buried InAs/GaAs quantum dots for direct measurements of In-Ga interdiffusion and In surface segregation lengths [1]. Here, we report cross-sectional scanning tunneling microscopy (XSTM) studies of In-In pair correlations within the wetting layers. In many high resolution XSTM images, we counted the number of In-In pairs along the [110] direction as a function of the spacing between them. Since

the number of In-In pairs greatly exceeds that for the random alloy, significant lateral In clustering within the wetting layers is apparent. In order to deduce an In-In pair interaction energy, we compared the experimentally determined fraction of In-In pairs with that for the random alloy. Interestingly, the nearest neighbor interaction energy is similar to that calculated for the first layer of a reconstructed dilute InGaAs alloy surface [2]. This suggests that lateral In clustering along the InAs wetting layer may be frozen in during growth, and that the wetting layer might provide a fast diffusion path for annealing-induced ordering of quantum dot arrays. In addition, we find similar In-In pair correlations and nearest neighbor interaction energies for wetting layers annealed at high temperatures, suggesting that the In atoms may prefer to diffuse in pairs.

- [1] B. Lita, R.S. Goldman, J.D. Phillips, and P.K. Bhattacharya, *Appl. Phys. Lett.* 75, 2797 (1999); *Surf. Rev. Lett.* 5, 539 (2000).
[2] J.-H. Cho, S. B. Zhang, and A. Zunger, *Phys. Rev. Lett.* 84, 3654 (2000).

R9.4
OPTICAL PROPERTIES OF SILICON NANOCRYSTALS. Zhonghua Yu, Lindsay Pell, Douglas English, Don O'Connor, Paul Barbara, Brian Korgel, Department of Chemistry and Biochemistry, Department of Chemical Engineering, Center for Nano- and Molecular Science and Technology, The University of Texas, Austin, TX.

Time- and wavelength-resolved luminescence as a function of temperature were used to investigate ensemble and single Si nanocrystals. These measurements offer new insights on the nature of luminescence from Si nanocrystals. Octanethiol-capped fluorescent Si nanocrystals, 2-10 nm in diameter and emitting visible light, were prepared in supercritical fluid. They have a fluorescence quantum yield of 5.5%, similar to previous silicon oxide-capped Si nanocrystals. Time-resolved single-photon counting measurement, both on bulk solution and single particles, gives a fluorescence lifetime of ~ 3.7 ns at room temperature, in contrast to microsecond lifetime in oxide-capped Si. An unexpectedly fast radiative rate on the order of 10^7 s⁻¹ is obtained for these organic-capped indirect-bandgap semiconductor nanocrystals, which is comparable to direct-bandgap CdSe nanocrystals. Narrow fluorescence of linewidth ~ 200 meV at room temperature are observed from individual particles, and emission is size-tunable from red to blue, strongly suggesting a quantum confinement mechanism. The optical properties were also investigated at variable low temperatures, providing further evidence for the nature of the emitting states in Si nanocrystals. A comparison of photophysics of Si nanocrystals vs. more conventional nanocrystals such as CdSe will be presented.

R9.5
PHOTOLUMINESCENT PROPERTIES OF CdSe NANOCRYSTALS IN THE PRESENCE OF AMINES. Baocheng Yang, Jeunghoon Lee, Rongfu Li, and Fotios Papadimitrakopoulos, Univ of Connecticut, Storrs, CT.

It was reported that the addition of hexadecyl amine to the synthesis of CdSe nanocrystals could sharpen their size distribution, increase their photoluminescence intensity and cause a recoverable blue shift of emission spectrum upon reintroduction of TOPO. At present, we used a series of amines to study the effect of basicity and steric hindrance on the photoluminescent spectra of CdSe nanocrystals as a function of size, concentration and time. Markedly different behavior in terms of PL peak-position and quantum yield were observed for primary amines versus secondary and tertiary amines. Although the latter amines caused similar blue shift of the PL position of CdSe nanocrystals, quantum yields of nanocrystals decreased, contrary to the primary amines case. In addition, it was shown that exchange temperature played a vital role in the ligand exchange process. The significance of our findings is elucidated with a newly developed model which is also compared to 'the dead-layer theory', previously used to account for fluorescent changes of CdSe single crystal upon exposure to various gaseous amines.

R9.6
CHARGE CARRIER GENERATION AND EXCITON QUENCHING AT M3EH-PPV/ OXIDE INTERFACES. Kathryn Brown, Physics Department, Colorado School of Mines, Golden, CO; Garry Rumbles, Brian Gregg, Phil Parilla, John Perkins, Alison Breeze, and David Ginley, National Renewable Energy Laboratory, Golden, CO.

Polymer based solar cells offer the potential for large area, low cost energy conversion. To accomplish this, carriers must be effectively generated and collected. The polymer/oxide interface plays a critical role in the decomposition of photo-generated excitons to charge carriers. We have initiated a series of experiments to examine the quenching behavior of a variety of organic and inorganic (oxide) interfaces on the luminescence in M3EH-PPV. We report on studies of the quenching behavior as a function of the nature of the oxide (electron affinity) for epitaxial or single crystal films and as a function

of surface roughness for nano oxides ink jet printed from colloidal and metal-organic precursors. We report on the photoluminescence for these films and compare the results with molecular quenchers such as metal phthalocyanines and perylene derivatives. We report on initial solar cells fabricated on the various oxide films.

R9.7
MORPHOLOGY AND ATOMIC STRUCTURE OF GRAIN BOUNDARIES IN GaN GROWN BY MOVPE. Eriko Takuma, Dept of Materials Science; Sakuntam Sanorpim, Kentaro Onabe, Dept of Applied Physics; Hideki Ichinose, Dept of Materials Science, Univ of Tokyo, Tokyo, JAPAN.

Morphology and atomic structure of hexagonal gallium nitride (h-GaN) grain boundary were investigated employing conventional TEM and atomic resolution high voltage transmission electron microscope (ARHVTEM), respectively. Selective area growth (SAG) of GaN was performed on a patterned GaAs (001) substrate by metalorganic vaporphase epitaxy (MOVPE). The mask pattern was aligned along $\langle 011 \rangle$ direction on a GaAs (001) substrate. Cubic GaN (c-GaN) was mainly grown in the window area of the patterned substrate. c-GaN in the window was mixed by polycrystalline hexagonal phase. Hexagonal GaN (h-GaN) was grown in the mask area. The h-GaN phases on both sides of the window area contacted during the growth to produce a $\Sigma 9$ CSL grain boundary, of which rotation angle and common axis were respectively 70.5 degrees and $\langle 1120 \rangle$. Several $\Sigma 9$ CSL boundaries were found in the h-GaN phase in the window area too. A grain boundary between the h-GaN phases of the window area and that of the mask area also produced $\Sigma 9$ CSL boundary. The boundary plane was in most cases symmetric and an asymmetric type followed. The symmetric boundary was parallel to (3308) plane of each crystal. The asymmetric boundary was parallel to (0001) and (3302) plane of the each component crystal. Atomic structures of these grain boundaries were investigated by ARHVTEM.

R9.8
OPTICAL PROPERTIES OF SEMICONDUCTOR NANOPARTICLES-INFLUENCE OF ORGANIC SURFACE PASSIVATION AND EMBEDDING MEDIUM. Jess Wilcoxon and Paula Provencio, Sandia National Laboratories, Albuquerque, NM.

A defining aspect of nanosize materials is the presence of an enormous fraction of surface atoms. These surface species and their chemical interactions with surface passivating agents affect properties like absorbance, photoluminescence, (PL) and magnetic response. Concepts employed in solid state physics which assume significant translational symmetry (e.g. direct vs. indirect bandgaps) become less relevant and inorganic clusters behave more like large molecules, with discrete densities of states. For this reason, the optical properties of even dilute dispersions of nanoclusters are strongly affected by the embedding medium. We discuss experimental studies of the effect of organic passivating agents and coordinating solvents on the absorbance and PL properties of semiconductor nanoparticles such as CdS, CdSe, and HgSe. Among the interesting results reported is a large dependence of the PL efficiency and energy on solvent, organic passivator, and also inorganic ions (e.g. Cd(II)). Perhaps, even more interesting is the significant effect of these interface factors on the absorbance excitonic features (e.g. linewidth), demonstrating that such features cannot be predicted just from the known the mass (size) of the cluster. Chemically specific chromatographic separation is used to demonstrate that even clusters with identical band-gaps, can have distinct chemical properties and absorbance features.

Acknowledgment:

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R9.9
STRUCTURAL STUDIES OF InAs-InP COUPLED MULTILAYER QUANTUM DOT SYSTEMS. R.L. Maltez, D. Ugarte, W. de Carvalho Jr., G. Medeiros-Ribeiro, Laboratorio Nacional de Luz Sincrotron, Campinas, BRAZIL.

In previous works we have studied the coupling of InAs and InP Quantum Dots (QDs) on a single bilayer using the InAs QDs layer as a template. We have observed that a GaAs spacer of 5 nm (between the QDs layers) improved the InP QD size dispersion, as measured by AFM images of uncapped samples. This spacer also provided a strong vertical alignment. Here, we have investigated structures consisting of stacks of four of such QD bilayers (QDBLs), as a function of selected growth parameters. The structures were grown on (001) GaAs substrates at 550°C using triethylgallium, trimethylindium, arsine and phosphine as the precursors on a commercial MOCVD reactor. Between QDBLs, a thin GaP cap (about 1 ML) covered the InP QDs layer, followed by a GaAs spacer. The samples were analyzed by TEM and AFM techniques in order to obtain a morphological map of the

system as a function of the InAs and InP coverage. TEM reveals extended defects beginning close to the islands and propagating up to the sample surface. The conditions for defect formation and the relative degree of vertical alignment are also mapped. The results also show an island size enlargement along [-110] direction as the QDBL number is increased. We have also investigated the changes on the structural quality of the system by varying the GaP cap thickness and the GaAs spacer thickness between bilayers. In summary, the results show that it is possible to stack alternate multilayers of InAs and InP vertically coupled QDs with no structural defects.

R9.10

CURRENT-VOLTAGE SCANNING TUNNELING SPECTROSCOPY AT ULTRASMALL Si NANOPARTICLES AS A FUNCTION OF PARTICLE SIZE. J. Therrien, A. Smith, M.H. Nayfeh, Univ of Illinois, Dept of Physics, Urbana, IL; L. Mitras, North Carolina State University, Raleigh, NC.

We use electrochemical etching to produce hydrogen capped spherical Si_n clusters of discrete sizes of diameter $d \sim 1.0$ (Si29), 1.67 (Si123), 2.15, and 2.9 nm diameter, which are then separated according to size using chromatography. The size and shape is determined using high-resolution transmission electron microscopy. Current-voltage spectra are recorded, for particles deposited on p-type Si, using scanning tunneling spectroscopy under light illumination from a mercury lamp. Resonance structure in the differential conductance is fitted by hole confinement model with the hole mass as a parameter. The fit gives a mass equal to the electronic free mass for $d = 1$, and 1.7 nm, but equal to 0.73 and 0.23 of the free mass for $d = 2.15$, and 2.9 nm respectively, indicating a transition from bulk-like mass to free mass.

R9.11

INVESTIGATION OF OXIDATION PROCESS OF ULTRATHIN FILMS OF AMORPHOUS AND/OR NANO-CRYSTALLINE SILICON. R. Mu, A. Ueda, M. Wu and D.O. Henderson, Chemical Physics Lab., Department of Physics, Fisk University, Nashville TN; A.B. Hmelo and L.C. Feldman, Department of Physics and Astronomy, Vanderbilt University, Nashville, TN; C.M. Lukehart, Department of Chemistry, Vanderbilt University, Nashville, TN.

Silicon oxides have been studied extensively due to its broad applications ranging from photonics to microelectronics. In many cases, the stable phase of silicon oxides, SiO₂ is the electrical insulator of the choice. It is especially true for silicon based components and devices. On the other hand, the oxides are also the common source of the component degradation as the result of defects and imperfection at the Si/SiO₂ interface. Up to now, most reported investigations of Si/SiO₂ interface have been limited to crystalline and amorphous silicon. The most profiling approaches are through careful removal of the oxide layer from the top surface. The uniformity of the removed or remained layer is critical and difficult to control. The situation gets more complicated when nano- and microcrystalline silicon materials are considered. In order to overcome these difficulties, we have used temperature controlled and highly sensitive quartz crystal microbalance (QCM) to address the oxidation issues under ambient conditions. Our primary interest is to study the oxidation process in thickness dependent amorphous silicon films and size-dependent nanocrystalline silicon films with the mass sensitivity better than 1ng or 10¹⁴ atoms/cm² for oxygen. The preliminary results show that the room temperature oxidation process of an amorphous silicon film is exponential. By gradually increase the film thickness, we are able to obtain the information on oxide layer thickness and its stoichiometry in depth from the absolute mass measurement. For thicker films, it can also be confirmed by RBS analysis.

R9.12

PHOTOLUMINESCENT AND ELECTROLUMINESCENT DEVICES BASED ON ZnS:Mn NANOCRYSTALS. Heesun Yang, Paul H. Holloway, Department of MS&E, University of Florida, Gainesville, FL; Banahalli B. Ratna, Center for Bio/Molecular Science and Engineering, Naval Research Laboratory, Washington, DC.

Doped nanocrystal semiconductor, a new class of luminescent material, has been demonstrated to have a much higher quantum efficiency for photoluminescence (PL) due to suppression of non-radiative recombination at defects and surface states. They have also been shown to have a luminescent decay rate several orders of magnitude faster than that of bulk crystals. The ZnS:Mn nanocrystals (NC) with sizes between 2 and 3 nm were synthesized via surface-capping organic material (p-thiocresol) as an inhibitor of crystal growth. The photoluminescent characteristics of a NC thin film, having a typical Mn²⁺ ⁴T₁-⁶A₁ transition, will be discussed in terms of shifts in excitation and emission wavelengths resulting from quantum confinement effects. A dc electroluminescent (EL) device having a unique multilayer structure, composed of ITO/PEDT-PSS/ZnS:Mn NC/Al and ITO/PEDT-PSS/PVK/ZnS:Mn NC/Al was

tested. Poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDT-PSS) plays a key role in enhanced hole injection, while poly(N-vinylcarbazole) (PVK) serves as both a passivation layer between PEDT-PSS/NC and a charge transport species. The orange color EL emission with wavelength of ~598 nm could be observed by eye, typically having a turn-on voltage of 5 V. Investigation of other device structures are in progress. Current-voltage and luminance-voltage characteristics of EL devices will be presented. In addition, the dependence of PL and EL characteristics on doping concentration of Mn from 0.5 to 5 mole % will be discussed.

R9.13

REM INVESTIGATION OF THE CORE/CLAD INTERFACE OF La₂O₃-Al₂O₃-SiO₂ GLASSES FOR HIGH POWER FIBER LASERS. Shang-Cong Cheng, Matthew J. Dejneka, Corning Inc, Science and Technology, Corning, NY.

For fabricating Yb³⁺ doped La₂O₃-Al₂O₃-SiO₂ glasses for high powered fiber lasers, it is critical to choose the right core glass composition to obtain a high NA and to avoid phase separation. TEM techniques were used to study the relationship between the core composition and phase separation. In the study, inter-diffusion between the core and clad glasses was found. The inter-diffusion caused phase separation in the region of the core/clad interface in fibers containing relatively high concentrations of La₂O₃. The TEM results were used to optimize the chemical composition of the core glass for high power fiber lasers.

SESSION R10: POSTER SESSION
ELECTRONIC MATERIALS
Wednesday Evening, April 3, 2002
8:00 PM
Salon 1-7 (Marriott)

R10.1

SYNTHESIS AND CHARACTERIZATION OF COMPOSITE LAYERED NANO-STRUCTURES. Daryush Ila, Robert L.

Zimmerman, Claudiu I. Muntele, Center for Irradiation of Materials, Alabama A&M University, Normal, AL; David B. Piker, Dale K. Hensley, Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN.

We have successfully synthesized nano-scale layered composites of gold-silica using two combined techniques of co-deposition and post irradiation [1] as well as ion implantation and post irradiation by MeV heavy ions [2]. In this process, we achieved a fine control in the size (0.5 to 10 nm), concentration (1% to 15%), and location of nanocrystals of Au in a silica host. We have also achieved a control in the layer thickness (1nm to 10 nm), separation of composite layers from each other. This fine control provides precision tool for optical device fabrication (multi-spectra-line filters) as well as for electro-optical device fabrications. To achieve this, we used the energy deposited due to the electronic excitation by post-implantation irradiation to induce the nucleation of nano-crystals with very short diffusion length. This process was used to reduce the diffusion length of gold into silica as well as to reduce the threshold concentration of gold needed to achieve such composites by at least two orders of magnitude. In this presentation, we will show the results obtained using silica-Au co-deposition along with post irradiation by 5 MeV Si beam and post annealing at various ambient and compare with the results obtained using Au implantation into silica followed by post annealing and/or post irradiation by MeV Si beam. The synthesis composite layered nano-structures were analyzed by optical absorption photo-spectroscopy, by electron diffraction, by transmission electron microscopy (TEM) and by Rutherford Backscattering Spectrometry (RBS).

Research sponsored by the Center for Irradiation of Materials, Alabama A&M University and the Division of Materials Sciences, U.S. Dept. of Energy, under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corp.

[1] Invited talk at the Surface Modification of Materials by Ion Beam Conference, Marburg, Germany, September 2001.

[2] Invited Talk at the Radiation Effects on Insulator Conference, Lisbon, Portugal (2001).

R10.2

Abstract Withdrawn.

R10.3

EFFECT OF OVERGROWTH ON SHAPE, COMPOSITION AND STRAIN OF SiGe ISLANDS ON Si(001). A. Hesse, J. Stangl, V. Holy, T. Roch, G. Bauer, University of Linz, AUSTRIA; U. Denker, O.G. Schmidt, MPI Stuttgart, GERMANY; O. Kirfel, D. Grützmacher, PSI Villingen, SWITZERLAND.

For the understanding of interdiffusion and the changes of the strain state during overgrowth of self-organized islands, a thorough investigation of the Ge island properties and their vicinity before and after Si capping is required. We use a method based on x-ray scattering experiments capable of resolving the shape and strain distribution in buried islands, as well as the composition distribution. Furthermore, strains in the Si matrix are obtained as well. The results on a series SiGe island samples are presented with Si cap layer thicknesses ranging from 1 to 30 monolayers. A significant interdiffusion, i.e., a lowering of the Ge content within the islands is found. With increasing cap layer thickness the elastic relaxation with respect to the initially uncapped islands is reduced. This is accompanied by an appreciable change of the shape of the islands, in agreement with transmission electron microscopy investigations.

R10.4

Ge-RICH $\text{Si}_{1-x}\text{Ge}_x$ NANOCRYSTAL FORMATION BY THE OXIDATION OF AS-DEPOSITED THIN AMORPHOUS $\text{Si}_{0.7}\text{Ge}_{0.3}$ LAYER. Tae-Sik Yoon, Ki-Bum Kim, School of MS&E, Seoul National University, Seoul, KOREA.

Ge-rich $\text{Si}_{1-x}\text{Ge}_x$ nanocrystals formation simultaneously with the formation of upper control oxide was proposed using the selective oxidation of Si during the dry oxidation process of amorphous $\text{Si}_{0.7}\text{Ge}_{0.3}$ layer. This process is for the application to flash type single electron memory device, which needs the thin tunneling oxide for low voltage operation, nanocrystals with a high spatial density for high threshold voltage shift, and upper control oxide with a good dielectric quality for stable operation of device. Therefore, the simultaneous formation of Ge-rich $\text{Si}_{1-x}\text{Ge}_x$ nanocrystals and thermally grown SiO_2 as upper control oxide by the dry oxidation of $\text{Si}_{0.7}\text{Ge}_{0.3}$ alloy film deposited on SiO_2 was investigated to satisfy the conditions of the high spatial density of nanocrystals and high dielectric quality of upper control oxide. Firstly, it was found that the oxidation kinetics of the alloy film in the temperature ranges from 600 to 800°C are well explained by the classical model proposed by Deal and Grove with the activation energies of the linear rate and parabolic rate regime of about 1.35 and 1.02 eV, respectively. As a result of selective oxidation process, Ge-rich $\text{Si}_{1-x}\text{Ge}_x$ nanocrystals are formed with the size of 5.6 ± 1.7 nm and with the spatial density of $3.6 \times 10^{11} / \text{cm}^2$ at 600°C. With increasing the oxidation temperature to 700 and 800°C, the size of nanocrystal is increased to about 20 nm. The size of nanocrystals as a function of temperature was explained considering the solid phase crystallization of amorphous film, oxidation rate, and the grain growth.

R10.5

SUB-NM COMPOSITION VARIATIONS IN Ge QUANTUM DOTS ON Si(100). Yangting Zhang, Margaret Floyd, Jeff Drucker, P.A. Crozier, David J. Smith, Arizona State University, Department of Physics and Astronomy and Center for Solid State Science, Tempe, AZ; K.P. Driver, Department of Physics and Astronomy, University of Louisville, Louisville, KY.

Higher growth temperatures during self-assembly of Ge quantum dots on Si(100) reduces the dispersion of dot sizes but activates Si interdiffusion. This interdiffusion alters morphological evolution and affects the optical and electronic properties of the dot ensemble. Electron-energy-loss spectroscopy (EELS) in a scanning transmission electron microscope was used to measure sub-nm composition variations in Ge/Si(100) islands grown by molecular beam epitaxy at substrate temperatures $400 \leq T \leq 700^\circ\text{C}$. These measurements were correlated with island ensemble morphology determined by atomic force microscopy (AFM). The average Si concentration of the islands and the Si/Ge interface width increased monotonically with growth temperature. Integrated island volumes measured by AFM were proportional to the equivalent Ge coverage, θ_{Ge} , with slopes greater than one for the higher deposition temperatures. This result confirms that the islands grow faster than the Ge deposition rate. Linear behavior of these island volume vs. θ_{Ge} curves implies that the average Ge composition is independent of island size. The volume at which islands change shape from pyramids to domes correlates well with the average Ge content of the islands in the context of simple strain-scaling arguments.

R10.6

THERMAL CONDUCTIVITY OF CARBON NANOTUBES PRODUCED BY MICROWAVE PLASMA CHEMICAL VAPOR DEPOSITION. Dajiang Yang, Qing Zhang, S.F. Yoon, J. Ahn, Sigen Wang, Qiang Wang, Microelectronics Centre, School of Electrical and Electronic Engineering, Nanyang Technological University, SINGAPORE.

We have measured the thermal conductivity of carbon nanotubes produced by microwave plasma chemical vapor deposition. The employed measuring method here is pulsed photothermal reflectance (PPR) technique. The thickness of the multi-walled carbon

nanotube films range from $\sim 10 \mu\text{m}$ to $\sim 60 \mu\text{m}$. Results show that the thermal conductivity of carbon nanotubes have no dependence on the length, and the value of the carbon nanotube thermal conductivity is comparable to that of diamond or in-plane graphite, while is less than theoretical predicted by Jianwei Che, Tahir Cagin, and William A. Goddard III. Our measurement technique is calibrated by measuring the silicon dioxide thermal conductivity.

R10.7

Re-OXIDATION OF SILICON (001) SURFACES AFTER MODIFICATION BY SELF-ASSEMBLING ORGANIC MONOLAYERS. Dario Narducci, Monica Bollani, Istituto Nazionale per la Fisica della Materia and Dept. Materials Science, Univ. of Milano Bicocca, Milan, ITALY; Laura Raimondi, Dept. Organic and Industrial Chemistry, Univ. of Milano, Milan, ITALY; Carole Fauquet-Ben Ammar, GPEC UMR CNRS 6631, Faculté des Sciences de Luminy, Université de la Méditerranée - Aix-Marseille II, Marseille, FRANCE.

Passivation of silicon surface toward oxidation represents a relevant issue in view of many microelectronic applications. In 2000 Chazalviel and co-workers [Surf. Sci. Lett., 444 (2000) L7] showed how molecular grafting with methyl groups could efficiently passivates atomically flat Si (111). No data are currently available on (001) surfaces, however, neither systematic analyses of the role played by the organic fragment on the passivation efficiency has been reported yet.

The aim of this communication is to present data on the passivation of (001) silicon surface by different aryl fragments self-assembled onto it. Passivation was carried out using electrophilic organic species that were let react onto a previously brominated Si surface. Specifically, six differently substituted phenyl groups were considered. The morphology of the surface after bromination was analyzed by AFM, its residual roughness evaluating typically to 0.8 nm over 5 mm - 5 mm surface areas. Six differently substituted phenyl groups were then grafted on the surface. These samples were characterized by attenuated total reflection and specular reflection infrared spectroscopy to detect the presence of arylc terminating groups. The kinetics of the re-oxidation reaction was then monitored over a time period of two months. We found two qualitatively different mechanisms of re-oxidation, depending on the structure of the organic fragment. The first mechanism is compatible with a model where the aryl group simply hinders the surface Si sites, disabling the access of oxidizing species to the surface itself, the kinetics being strongly reminiscent of that observed on hydrogen-terminated Si surfaces. The second process appears to be more complex, with the aryl group interacting with the oxidizing species and eventually activating it prior to its adsorption onto Si. In all cases, however, kinetics analyses lead to the conclusion that a significant portion of the silicon surface remains stabilized against oxidation.

R10.8

SnGe QUANTUM WIRE AND Sn QUANTUM DOT FORMATION VIA PHASE SEPARATION. Regina Ragan and Harry A. Atwater, California Institute of Technology, Pasadena, CA.

$\text{Sn}_x\text{Ge}_{1-x}$ alloys exhibit an indirect to direct energy bandgap transition for compositionally homogeneous alloys at $x > 0.10^1$ with applications as a Si-compatible, low cost thermophotovoltaics and near and mid-IR detectors. The incorporation of Sn in a Ge matrix is not thermodynamically favorable due limited bulk solid solubility. During molecular beam epitaxy of 1 micron thick $\text{Sn}_x\text{Ge}_{1-x}$ alloy thin films on Ge(001) with a growth temperature of $T = 160^\circ\text{C}$ and a growth rate of 3 nm/min, the morphology evolves into a dense array of $\text{Sn}_x\text{Ge}_{1-x}$ quantum wires oriented perpendicular to the substrate plane. The modulation of the alloy composition is evident in cross section transmission electron microscopy for film thickness ranging from 0.5 to 1 μm . For the $\text{Sn}_x\text{Ge}_{1-x}$ alloy with $x = 0.03$, the lateral composition modulation has a period of 23 nm. Further analysis using scanning transmission microscopy in planar view yields a Sn composition in the Sn-rich wires of approximately $x = 0.06$. TEM analysis indicates that the phase separation occurs within coherent films and is not related to dislocation formation. Fourier transforms of atomic force microscopy images shows the preferred wavelength for the phase separation. This preferred wavelength is compared to both thermodynamic² and kinetic models.³ *Ex-situ* annealing at $T = 550^\circ\text{C}$ to 650°C of the 1 μm thick $\text{Sn}_x\text{Ge}_{1-x}$ alloys induces a dramatic change in the film morphology. Sn segregates and forms quantum dots with diameters dependent on the annealing temperature, 7 nm at 550°C and 30 nm at 650°C , with a 20% variation in the size distribution. The crystal structure of the quantum dots is investigated with HR-TEM and diffraction pattern analysis. FTIR spectroscopy transmittance of these phase separated alloys has an absorption edge dominated by the Sn rich regions.

¹ R. Ragan and H.A. Atwater, App. Phys. Lett. 77, 3418 (2000).

² F. Glas, Phys. Rev. B 55, 11277 (1997).

³ B.J. Spencer, P.W. Voorhees, and J. Tersoff, Phys. Rev. Lett. 84, 2449 (2000).

R10.9

OPTICAL AND STRUCTURAL STUDIES OF SILICON LOW-DIMENSIONAL WIRES AND DOTS. T.V. Torchynska, Francisco Guillermo Beseril Espinoza, Faculty of Physics and Mathematics, National Polytechnic Institute, MEXICO DF.

The mechanisms of the photoluminescence in silicon low-dimensional wires and dots are discussed. Comparative investigations of the photoluminescence (PL) and its excitation (PLE) peculiarities in Si wires, like porous silicon (PSi), and silicon quantum dots (QD/s) embedded in silicon oxide films using magnetron co-sputtering method have been analysed. Photoluminescence (PL), photoluminescence excitation (PLE), Raman scattering, IR absorption, X-ray electron photoemission (XPS) and electronic paramagnetic resonance (EPR) spectroscopies, as well as scanning electron microscopy (SEM) and atomic force microscopy (AFM) were used in present work to study of the photoluminescence mechanisms in above-mentioned systems. We have found that bright red photoluminescence in PSi can be decomposed in to the two elementary luminescence bands: A (1.70-2.0 eV) and B (2.0-2.1 eV) with specific PL excitation spectra. The relative intensities of the A and B bands have changed with the variation of the preparation condition, as well as with the variation of the temperature of measurements and wavelength of the excitation light. The very bright A band dominates in the PL spectra for PSi samples with the low-dimensional structure on the top surface characterized by size of the 20-100nm and height of 10-30 nm, as well as, the largest Si/SiO_x interface area. It has been shown that the PL spectra of the Si (QD/s) in silicon oxide also are characterized by the two luminescence bands peaked at 1.6-2.0 eV and 2.0-2.2 eV. The intensity of former one increases with Si quantum dots appear in the silicon oxide. New conception of the effective photoluminescence in Si wires and dots was developed [1]. This conception based on ballistic effect realisation in low-dimensional Si structures.

1. T.V. Torchynska, M. Morales Rodriguez, F.G. Bacarril-Espinoza, N.E. Korsunskaya, L. Yu. Khomenkova, L.V. Scherbina, Ballistic effect and red photoluminescence of Si wires. Phys.Rev.B (USA), 2001.

R10.10

PHOTOLUMINESCENCE EXCITATION MECHANISM IN Si WIRES AND DOTS. F.G. Becerril Espinoza, T. Torchynska, J. Aguilar Hernandez, A.I. Diaz Cano, Faculty of Physics and Mathematics, National Polytechnic Institute, MEXICO; Y. Goldstein, A. Many, J. Jedrzejewski, Racah Institute of Physics, Hebrew University of Jerusalem, ISRAEL; B.M. Bulakh, L.V. Scherbina, Institute of Semiconductor Physics National Academy of Sciences, Kiev, UKRAINE.

Photoluminescence (PL), their temperature dependencies, as well as Raman scattering spectra of porous silicon (PSi) and Si quantum dots (QD/s) embedded in silicon oxide (by magnetron co-sputtering method) have been investigated. PL band of PSi characterised by the peak 1.7-1.9 eV (A) at T=300K. The PL spectrum changes with decrease of temperature up to 150K due to increase the high energy part of luminescent band. The PL spectra at 8.5-150K could be decomposed on two overlapping Gaussians: previous one and new one peaked at 1.90-2.00 eV (B). PL spectra of Si QD/s embedded in silicon oxide also are characterised by two bands peaked at 1.6-1.8 and 2.10-2.20 eV. Raman scattering spectra have shown Si QD/s existed in silicon oxide annealed at T=1100 °C only. The comparative investigation of PL peculiarities in peculiarities on PSi and silicon oxide (with and without Si QD/s) has been used for confirmation of defect related luminescence models for some investigated elementary luminescence bands. The photoluminescence excitation mechanism changes with Si QD/s appearance in silicon oxide will discuss as well.

R10.11

PASSIVATION AND FUNCTIONALIZATION OF NANO-STRUCTURED SI(111). A. Kirakosian, J.N. Crain, J.-L. Lin, J.L. McChesney, F.J. Himpel, Dept of Physics, Univ of Wisconsin-Madison, WI; Y. Gu, N.L. Abbott, Dept of Chemical Engineering, Univ of Wisconsin-Madison, WI.

Vicinal Si(111) 7×7 surfaces form well-organized step arrays with periodicities ranging from 6 to 80 nm [1]. Such patterned surfaces are possible templates for self-assembled nanostructures, such as arrays of molecular switches and biosensors utilizing oriented liquid crystals. However, clean silicon exposed to a molecular solution oxidizes into a rough surface and the step pattern prepared under vacuum is lost. A continuous gold film deposited on a Ti wetting layer replicates the step morphology faithfully within 0.28 nm, as determined by STM [2]. The gold not only passivates the surface, but at the same time, functionalizes it for the adsorption of thiol-derivatives of organic molecules and biomolecules. Coverage and orientation of alkanes and DNA adsorbed on such functionalized surfaces are determined by polarization-dependent absorption spectroscopy from the C 1s and N 1s core levels [3]. An anisotropy perpendicular to the surface is found.

[1] J.-L. Lin, et al., J. Appl. Phys. 84, 255 (1998); A. Kirakosian, et al., Appl. Phys. Lett. 79, 1608 (2001).

[2] A. Kirakosian, et al., J. Appl. Phys. 90, 3286 (2001).

[3] J.N. Crain et al., J. Appl. Phys. 90, 3291 (2001).

R10.12

Abstract Withdrawn.

SESSION R11: NANOSTRUCTURED INTERFACES IN ELECTRONIC MATERIALS I

Chair: Hideki Ichinose

Thursday Morning, April 4, 2002

Salon 5/6 (Marriott)

8:00 AM *R11.1

GROWTH, STRUCTURE AND FUNCTIONALITY OF SEMI-CONDUCTOR NANOCRYSTALS THROUGH Z-CONTRAST MICROSCOPY AND THEORY. S.J. Pennycook, A. Kadavanich, A. Franceschetti, S.T. Pantelides, Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN and Dept. of Physics and Astronomy, Vanderbilt University, Nashville, TN; A.R. Lupini, Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN; J.R. McBride, S.J. Rosenthal, Dept. of Chemistry, Vanderbilt University, Nashville, TN; R.C. Puetter, A. Yahil, Pixon LLC, Stony Brook, NY.

It is well known that quantum confinement effects in semiconductor nanocrystals are the origin of the size-dependent electronic and optical properties and their many potential applications in optics, electronics and catalysis. However, to understand nanocrystal functionality at a fundamental level requires more detailed knowledge of surface termination, stoichiometry and the presence of special sites such as vacancies that might act as traps for carriers or active sites for catalysis. The combination of atomic-resolution Z-contrast scanning transmission electron microscopy (STEM), electron energy loss spectroscopy (EELS) and first-principles theory is very effective in unraveling the origin of functionality in nanostructures. Z-contrast imaging of nanocrystals allows reconstruction of the three-dimensional shape. In the case of chemically-synthesized CdSe nanocrystals, the shape is asymmetric reflecting the polarity of the crystal. Images of core shell nanocrystals show directly the extent of the core. Such information is an excellent starting point for first-principles theoretical studies. As an example, we show that photocatalytic fixation of CO₂ by CdSe nanocrystals does not occur at a surface site at all, but by the injection of highly reactive CO₂- radicals into solution where they can react and 'fix' other CO₂ molecules. Determining nanocrystal functionality will be greatly facilitated by the reduced probe sizes after correction of objective lens spherical aberration, when we anticipate single atom sensitivity for imaging and perhaps also for the detection of impurities or dopants by EELS.

8:30 AM *R11.2

AB INITIO INVESTIGATIONS OF TRANSPORT THROUGH CLUSTER-BASED MOLECULAR SYSTEMS. Christopher Roland, Vincent Meunier, Department of Physics, NC State University, Raleigh, NC; Brian Larade, Jeremy Taylor and Hong Guo, Department of Physics, McGill University, Montreal, P.Q. CANADA.

The recent advent of moletronics has opened up a new frontier, whose aim is the ultimate miniaturization of electronic devices. Work in this field has clearly demonstrated that many of the important device characteristics relate specifically to the strong coupling between the atomic and electronic degrees of freedom. Using a recently developed formalism that combines the Keldysh non-equilibrium Greens functions with ab initio theory, we have directly simulated the current-voltage (I-V) characteristics of several prototypical nanoscale device systems. Specific systems considered here will include Si and Na clusters coupled to both Al and Au leads, as well as fullerene-based systems. The I-V signatures of these nanocluster systems is understood in terms of a significant transfer of charge between the clusters and electrodes, and the couplings between the electrode bands and the energy levels of the nanoclusters.

9:00 AM R11.3

THE CORE STRUCTURE OF A 30 DEGREE PARTIAL DISLOCATION IN GaAs: MERGING THEORY AND EXPERIMENT QUANTITATIVELY. X. Xu, C. Kisielowski, National Center for Electron Microscopy (NCEM), Lawrence Berkeley National Lab. (LBNL), Berkeley, CA; P. Specht, E.R. Weber, S.F. Beckman, D.C. Chrzan, Materials Science and Engineering, University of California, Berkeley, CA.

In recent years it became possible to extend the resolution of field emission microscopes into the sub Angstrom region by reconstruction of the electron exit wave from a focal series of lattice images. Thereby, it is now feasible to investigate defects and interfaces on a truly

atomic scale in many materials systems. On the other hand, progress in theory enables scientists to calculate the total energy configuration of systems that are comparable in size with what is typically investigated by high-resolution transmission electron microscopy. Therefore, a quantitative investigation of the agreement between theoretical calculations and experiments is feasible. In this contribution we investigate the core structure of a 30-degree partial dislocation in low temperature grown GaAs:Be. Ab initio electronic structure total energy calculations are used to compute the expected structure for both the Ga-centered and the As-centered 30 degree partial dislocation cores in GaAs. NCEM's One Angstrom Microscope with an information limit of ~ 0.08 nm is used to image this structure. It is shown that it is possible to discriminate between Ga and As columns in phase contrast microscopy if wedge shaped samples are utilized. The agreement between theory and experiment is tested by a determination of the column position in - and around the dislocation core with pico meter precision. The agreement between experiment and theory is remarkable. Currently, strain relaxation and column bending in the ~ 5 nm thin TEM foil are major sources of difference between calculations and experiments and they are accessed quantitatively.

9:15 AM R11.4

QUANTITATIVE HIGH-RESOLUTION TRANSMISSION ELECTRON MICROSCOPY OF III-V SEMICONDUCTOR INTERFACES BY MULTIVARIATE STATISTICAL ANALYSIS OF EXIT-PLANE WAVE FUNCTION IMAGES. K. Mahalingam, K.G. Eyink, G.J. Brown and D.L. Dorsey, Air Force Research Laboratory, Materials & Manufacturing Directorate, Wright-Patterson Air Force Base, OH.

The current techniques for quantitative atomic-scale chemical mapping of interfaces in III-V semiconductor heterostructures by high-resolution transmission electron microscopy (HRTEM) are typically restricted to ternary systems with intermixing in only one sublattice (either the group-III or group-V sublattice). They further require images obtained under optimum specimen-thickness and imaging conditions, which depend on the system being investigated. Recently, there has been significant progress in experimental and computational techniques to retrieve the electron wave function at the exit surface of the specimen. The analysis of exit-plane wave function (EPW) images offers important advantages over existing methods, since it permits the analysis of both group-III and -V sublattices and further eliminates artifacts (such as image delocalisation) arising from the imaging system. In this study we examine the application of EPW (amplitude and phase) images for an atomic-scale compositional mapping of interfaces in the GaAs-AlAs system. Image simulations based on the multislice algorithm were performed to obtain EPW images over a wide range of compositions and specimen thicknesses. Several methods, based on multivariate statistical analysis, were employed on both amplitude and phase images to de-couple image contrast due to change in composition from that due to change in thickness. Further details on the comparison of results obtained in this study with those obtained based on previous methods will be presented. Extension of this approach to systems with intermixing in both sublattices, viz. the InAs-GaSb system, will also be presented.

9:30 AM R11.5

ATOMIC STRUCTURE OF FIVE FOLD TWIN CENTERS IN DIAMOND FILM. Hidetaka Sawada, Hideki Ichinose, Univ of Tokyo, Dept of Materials Science, Tokyo, JAPAN.

Diamond has been recognized as a promising wide-gap-semiconductor material for the various applications in the harsh environment. Since the property of the crystal is suffered from growth defects, strong interest was put on it. In this study, atomic resolution high voltage transmission electron microscopy was applied on a fivefold twin structure, which corresponded to 7.4 degree disclination. The manner of stress accommodation shared by the five crystals is keenly interested. A diamond film 1.0-2.0 μ m in thickness was grown by microwave-plasma CVD at the condition of 0.5 % CH₄ / H₂. A specimen for HRTEM was prepared by focused ion beam (FIB) method. The core structure of the fivefold twin shown by the HRTEM image supported the structure model suggested by Matsumoto and Matsui i.e. No dangling bond was necessary to build up this structure. The core tube consisted of a five fold membered ring. The disclination angle was not equally shared by the five twins. Disorientation of the boundary depended on the growth direction of the film.

10:15 AM *R11.6

AB-INITIO CALCULATION OF DOPANT SEGREGATION AT SILICON-DIELECTRIC INTERFACES. Wolfgang Windl, Ohio State Univ, Dept of Materials Science and Engineering, OH.

The progressing miniaturization of semiconductor devices continuously increases the dependence of the device properties on the interfaces between the different gate stack materials. By now, SiO₂ dielectric

layers have been reaching a thickness of less than 2 nm, and currently studied ultra-thin body silicon-on-insulator MOSFETs can have silicon channel layers that are only a few nm thick. In this situation, it becomes crucial to know how common dopants interact with the different interfaces. Segregation of dopants from one side of the interface to the other as well as dopant pile-up at the interface are possibilities. Whereas it seems that the latter has been observed experimentally for As at the Si/SiO₂ interface [Kasnavi *et al.*, J. Appl. Phys. **78**, 2255 (2000)], dopant-interface interactions are generally not well known, especially for interfaces with new gate-stack materials such as high-k oxides. In this paper, we will examine the interaction between some common dopants and interfaces between silicon and dielectric materials using ab-initio electronic structure calculations. We will show that the specific atomic structure of the interface influences strongly the segregation behavior of the different dopants, and will discuss its influence on the device properties.

10:45 AM R11.7

HETEROGENEITY OF SiGe NANOSTRUCTURES ON PATTERNED ULTRATHIN SOI. E.R. Tevaarwerk, O.M. Castellini, D. Keppel, M.A. Eriksson, P. Rugheimer, D.E. Savage, M.G. Lagally, University of Wisconsin-Madison, Madison, WI.

Thinned SOI (5 nm silicon) is patterned into square mesas with widths ranging from 5 to 20 nm. Silicon-germanium quantum dots (QDs) are grown by CVD and MBE. Because the silicon-silicon dioxide interface is a maximum of 5 nm from the QDs, the interface dominates the QD properties. The QDs nucleate in concentric rings beginning at the edge of the mesas and vary in size across the mesas, with the largest QDs found at the edge. Atomic force microscopy and transmission electron microscopy measurements reveal that the QDs in the outer rings are separated from one another by oxide, indicating incorporation of the surrounding silicon into the QDs. QDs in the center of the mesa are connected to one another by a silicon layer, suggesting less incorporation of the original silicon layer into the QDs. Electric force microscopy (EFM) confirms that the edge QDs are electrically isolated from the other QDs on the mesa. Surprisingly, EFM also allows us to resolve boundaries between QDs better than intermittent-contact AFM. Contact electrification is used to deposit charge on and off the mesas. Charge deposited on a mesa spreads to cover the majority of the mesa but remains confined to the mesa. Charged deposited off the mesas, where no silicon is present, remains localized to the contact point. Finite-element calculations of the tip-sample electrostatics explain how the nanostructured surface modifies the electrostatic force gradient on the EFM tip. This work supported by the NSF and ARO.

11:00 AM R11.8

HIGH RESOLUTION STUDY OF INTERFACIAL LAYER FORMATION MECHANISMS IN HIGH-K DIELECTRIC MATERIALS. Nabil Bassim, Valentin Craciun, Kerry Siebein, Rajiv K. Singh, University of Florida, Department of MS&E, Gainesville, FL.

As device scales for microelectronics decrease, the conventional gate dielectrics, thermally grown SiO₂ and oxynitride materials, are reaching their limits due to the development of high leakage currents caused by direct electron tunneling as these devices get thinner. One set of possible replacements proposed are high-k oxides which could maintain the same capacitances with a larger physical thickness. The development of a low-k interfacial reaction layer between the Si substrate and the deposited high-k films have slowed their development as suitable alternatives. According to our previous studies, the rapid diffusion of silicon atoms from the substrate as well as the presence of physisorbed oxygen in the deposited oxide films have led to a complex intermixing of these elements together with those of the grown film during the formation of the interfacial layer. A detailed structural and chemical study across the width of this layer could be an important contribution to the understanding of the interfacial layer growth mechanisms. In this study, we used high-resolution analytical electron microscopy to study these formation mechanisms in conjunction with x-ray photoelectron spectroscopy and x-ray reflectivity for the medium-k dielectric materials, yttria and zirconia. It is shown the the composition of the interfacial layer depends on substrate temperature and oxygen pressure during deposition.

11:15 AM R11.9

Abstract Withdrawn.

11:30 AM R11.10

NANO-STRUCTURE TRANSFER IN SEMICONDUCTORS BY ION EXCHANGE. L. Dloczik, R. Könenkamp, Hahn-Meiter Institut Berlin, Berlin, GERMANY.

We report the transfer of nano-structures in compound semiconductors by chemical ion exchange. Using a columnar nano-

structure given by a thin film of free-standing, vertically aligned ZnO columns (1), it is demonstrated that this structure can be transferred to ZnS, Cu₂S, Ag₂S, Sb₂S₃, Bi₂S₃, and other compounds with no change in morphology. The chemical process underlying this morphology transfer is the reactive exchange of ions between the solid and ionic solutions or reactive gases. In the compounds investigated, both, the chalcogen and the metallic ions can be exchanged. The processes involve temperatures below 400°C and are compatible with large area applications. When the reaction kinetics are sufficiently well controlled, one can also achieve a partial ion exchange. This opens the way to an accurate manipulation of nano-structures. We demonstrate that a partial ion exchange lends itself to the preparation of tubular structures with wall thickness as low as a few nanometers. Thin films of nearly vertically aligned tubes were prepared for all compounds listed above. Applications for these novel films include optical coatings, photovoltaic substrates, sensors and field emitters. (1) L. Dloczik, R. Engelhardt, K. Ernst, S. Fiechter, I. Sieber, and R. Knekamp, Appl. Phys. Lett. 78, 3687 (2001).

11:45 AM R11.11

DIRECT ELECTRON BEAM PROCESSING OF SEMI-CONDUCTOR NANOSTRUCTURES. Yeonjoon Park, Rian Zhao, Eicke R. Weber, U.C. Berkeley, Materials Science Engineering Department, Berkeley, CA.

Nanofabrication is one of the most interesting and challenging issues in semiconductor materials science and industry today. A topic of special interest in this field is the development of nanostructure processing techniques that do not rely on lithography. Using a focused electron beam we succeeded in direct e-beam patterning of a GaAs substrate without any resist materials. An in-situ high beam-current secondary electron microscope with a special vibration compensation capability was built in UHV-connection with a molecular beam epitaxy (MBE) chamber. A focused electron beam with a high beam-current of 100nA in a 20nm beam-spot size was used to create sub-micron surface structures on GaAs. Small craters of a few hundred nano-meter size were formed in very short time, between micro-seconds and milli-seconds each. A successive post-annealing in the MBE chamber under As over-pressure was performed to reduce the e-beam irradiation damage. The properties of these nano-craters are investigated with various methods. Possible applications of this novel fabrication technique will be discussed.

SESSION R12: NANOSTRUCTURED INTERFACES
IN ELECTRONIC MATERIALS II
Chairs: Eric A. Stach and Gerd Duscher
Thursday Afternoon, April 4, 2002
Salon 5/6 (Marriott)

1:30 PM *R12.1

STRUCTURE AND PROPERTIES OF DEFECTS AT THE SiC-SiO₂ INTERFACE. Alberto Franceschetti, S.T. Pantelides, Department of Physics and Astronomy, Vanderbilt University, Nashville, TN; and Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN.

Defects at the SiC-SiO₂ interface determine the performance of SiC-based devices, but their atomic-scale structure and properties have remained elusive. We report first-principles density-functional calculations in terms of which we identify the main possibilities: Si-Si suboxide bonds lead to gap states near the conduction-band edge, while carbon precipitates lead to states near the valence-band edge and to dangling-bond states in the upper part of the band gap. The effect of hydrogen and nitrogen passivation on these defects is analyzed in the context of relevant experimental data.

2:00 PM *R12.2

ATOMIC AND ELECTRONIC STRUCTURE OF INTERFACES AT SiC STUDIED BY INDIRECT HRTEM AND IMAGING SPECTRUM. Fu-Rong Chen¹, Hideki Ichinose², J.J. Kai¹, Eriko Takuma² and J.Y. Yan¹. ¹Center of Electron Microscopy, Dept. of Engineering and System Science, National Tsing Hua University, Hsin Chu, TAIWAN. ²Department of Materials Science, School of Engineering, The University of Tokyo, JAPAN.

Obtaining electronic and atomic structure of material simultaneously is very important for developing the nano-technology. In this paper, we demonstrate that atomic and electronic structure of an interface can be extracted with combination of Gerchberg-Saxton indirect microscopy and imaging spectrum technique. Basically, Gerchberg-Saxton algorithm includes two projections. Projection in the real space is a maximum entropy (ME) de-convolution process and in reciprocal space is an amplitude substitution process. It has been shown that Gerchberg-Saxton algorithm can extend the structural resolution to near 0.1nm [1,2]. Imaging spectrum technique coupling with FFT interpolation and maximum entropy de-convolution has

been shown to be useful to map the dielectric function for low-k materials [3]. With our recent development of wavelet transformation we apply imaging spectrum to map the sp²/sp³ distribution [4]. The spatial resolution of imaging spectrum is near 1 nm now, and we intend to push this technique to near atomic resolution level. Grain boundary and interface at SiC are good candidates for this study, since the bond distance of Si-C is slightly less than 0.1nm which is not routinely resolvable using a FEG TEM and Si-L (99eV) and C-K-edges (283 eV) locate in a reasonable energy range. The resultant electronic structure can be also compared with that calculated using WIEN97. The detail result of both electronic and atomic structure and the detail analysis techniques will be presented in the conference. Ref: 1. F.R. Chen, H. Ichinose, J. Kai and L. Chang, J. of Elec. Micros. (2002), 50, pp. 2. F.R. Chen, J.J. Kai, L. Chang etc., J. of Elec. Micros. (1999), 48, pp 827-836. 3. S. Lo, J.J. Kai, F.R. Chen, etc., J. of Elec. Micros. (2002), 50, pp. 4. J.Y. Yan, F.R. Chen, J.J. Kai, in preparation to J. of Elec. Micros.

2:30 PM R12.3

ATOMIC AND ELECTRONIC STRUCTURE OF THE {112} Σ₃ GRAIN BOUNDARY OF DIAMOND AND SILICON. Hideyuki Sawada, Hideki Ichinose, the Univ of Tokyo, Dept of Materials Science, Tokyo, JAPAN; Masanori Kohyama, AIST Kansai, Special Division of Green Life Technology, Osaka, JAPAN.

A grain boundary in diamond shows characteristic feature compared to other covalently bonded materials such as silicon even though these materials are common in crystal structure. The characteristic feature of diamond grain boundary is attributable to electronic structure of carbon. In order to understand the correlation between the electronic structure and the atomic structure in the grain boundary, the both atomic and electronic structure of the {112} Σ₃ CSL boundary of silicon and diamond was investigated in atomic dimension. The {112} Σ₃ boundary was produced in a CVD diamond films grown on a synthetic Ib diamond (001)-substrates by microwave-plasma method. The film was sliced by focused ion beam (FIB) method to be parallel to the {110} plane. Then damaged surface layer of the specimen was removed by low acceleration voltage operation of Ar ion milling. Atomic structure observation was carried out employing JEM-ARM1250 high voltage high-resolution transmission electron microscope of the University of Tokyo. Spherical and chromatic aberration constants of the microscope are respectively C_s = 1.4mm, C_c = 2.5mm. Information limit of the microscope extends over 0.1nm. Two characteristic structures were observed in the diamond boundary. One showed asymmetric structure and the other showed symmetric structure. The both consisted of the 5-6-7 membered rings. The single atomic column, which consists of three-fold coordinated atom, was identified by our super high-resolution of the present microscope. Electronic structure was calculated by the ab-initio molecular dynamic method using a plane-wave pseudopotential based on the density-functional theory. The calculated electronic structure was compared with the result of electron energy loss (EELS) spectroscopy. The EELS line corresponded to 1s_{π*} transition in the {112} Σ₃ grain boundaries. The ab-initio calculation showed that the π* line was attributed to three-fold coordinated atom in the boundary.

3:15 PM *R12.4

SURFACE POTENTIAL MAPPING OF PATTERNED SAMS BY SCANNING PROBE MICROSCOPY. Dawn A. Bonnell, Rodolfo Alvarez, Dept of MS&E, University of Pennsylvania, Philadelphia, PA; Kenneth G. Sharp, Simona Percec, Paula B. Hietpas, R. Ross Getty, DuPont Experimental Station, Wilmington, DE.

Surface potentials of a number of patterned conducting and insulating self-assembled monolayers (SAMs) were measured by scanning probe microscopy as part of a study in molecular electronics. Differences in surface potential were measured for thioalkanes on gold and alkylsilanes on SiO₂. The SAMs were patterned by micro-contact printing. High contrast patterns were observed by surface potential even when little imaging was possible in normal AFM modes. The potential gradients in SAMs around a charged electrode were observed and measured to obtain an indication of the electrical characteristics of SAMs of several different compositions. Surface potential differences of a few mV to 500mV were observed under ambient conditions between adjacent SAMs of different compositions or between SAMs and the bare substrate. The relationship between surface potential and molecular properties will be developed.

3:45 PM R12.5

FIELD EMISSION CHARACTERISTICS OF CARBON NANOTUBES SYNTHESIZED BY C₃H₄ AND NH₃ GASES. Taewon Jeong, Jae Hee Han^{*}, Whikun Yi, SeGi Yu, Jeonghee Lee, Jungna Heo, Chang Soo Lee, Ji-Beom Yoo^{*}, and J. M. Kim The National Creative Research Initiatives, Center for Electron Emission Source, Samsung Advanced Institute of Technology, Suwon, KOREA.

*Center for Nanotubes and Nanostructured Composite,
Sungkyunkwan University, Suwon, KOREA.

We have successfully synthesized multiwalled carbon nanotubes (CNTs) by plasma enhanced chemical vapor deposition onto Co sputtered glass at 550°C in a gas mixture of propyne (C_3H_4) and ammonia (NH_3) as carbon precursor. Raman spectra confirmed the formation of carbon nanotubes as well as disordered graphitic layers on the wall surface. The growth condition and formation mechanism of CNTs using a C_3H_4 gas are under investigation with the possibility that three carbon containing C_3H_4 can be converted directly to hexagon of CNT by combining two molecules. As the flow rate ratio of NH_3 to C_3H_4 increased in the mixture gas, the geometry and alignment of CNTs were improved, which was confirmed by scanning electron microscopy. In addition, the field emission characteristics of CNTs were also improved — the turn on voltage became lower, and the current density and the field enhancement factor were more increasing. Therefore, the NH_3 gas flow rate ratio to the C_3H_4 gas was found to be an important factor to govern the geometric shape and field emission characteristics of CNTs.

4:00 PM R12.6

CARBON NANOTUBES: CHEMICAL AND STRUCTURAL EFFECTS OF FIB-ASSISTED Pt CONTACTS DEPOSITION.

K. Dovidenko, K.A. Dunn, School of Nanosciences and Engineering, UAlbany Institute for Materials, University at Albany-SUNY, Albany, NY; N.L. Abramson, Union College, Schenectady, NY; Y. Zhao, Physics Department, Rensselaer Polytechnic Institute, Troy, NY.

Carbon nanotubes make excellent novel candidates for the interconnect applications and for new type of devices. Besides the high mechanical strength combined with good heat conductance, carbon nanotubes have a variety of attractive electrical properties. Focused Ion Beam (FIB) instrument is often used to fabricate metal contact lines for electrical measurements on carbon nanotubes (CNTs), and for device nanoengineering. The quality of the interface between CNT and the metal contact line is of high interest, as the 30 kV focused Ga ion beam of the FIB can produce sufficient surface modification to alter the device performance or affect the measurements. We have used the FIB instrument to both fabricate the metal contacts and to make the electron-transparent samples across the Pt/CNT/ SiO_2 structure for further studies via transmission electron microscopy, energy dispersive x-ray analysis, electron energy loss spectroscopy and energy filtered imaging. The results of the effects of Pt deposition on the shape and composition of the top-most layers of the CNTs and the SiO_2 surface as a function of Pt deposition and FIB imaging parameters are presented.