Final report: DOE Grant No. DE-SC0001031 for Symposium HH, "Quantitative Characterization of Nanostructured Materials" April 13-16 2009.

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Symposium HH

Accurate knowledge of atomic arrangements in nanostructured materials is a key to understanding their physical properties. Unfortunately, traditional structure-solving approaches that assume long-range structural periodicity and rely upon Bragg reflections observed by X-ray/neutron diffraction methods fail on the local scale. Multiple experimental techniques exist for probing local atomic arrangements. Nonetheless, finding accurate comprehensive structural solutions for nanostructured materials still remains a formidable challenge because any one of the existing methods yields only a partial view of the local structure. Symposium HH "Quantitative Characterization of Nanostructured Materials" held April 13-16 at the 2009 MRS Spring Meeting in San Francisco, California, was motivated by the current lack of effective and robust measurement solutions to this truly interdisciplinary problem. The symposium's goal was to bring together experts in a wide variety of techniques used to probe the structure

of nanomaterials, with an eye towards fostering collaborations that would combine techniques and thus provide better constraints on the nanostructure. About 85 presentations, including 12 invited speakers, 48 contributed talks, and 25 posters, highlighted the state-of the art in nanostructure investigations using various x-ray/neutron scattering techniques (total scattering, small-angle scattering, COBRA), scanning probe microscopy (STM, AFM) for surface characterization, structural and compositional imaging in TEM, local electrode atom probe (LEAP); x-ray absorption fine structure (XAFS), neutron pair distribution function (PDF) analysis, NMR, Raman, and mass spectroscopy. Several presentations focused on the use of theoretical first principles calculations to interpret experimental measurements. Financial support of this symposium was provided by the MRS and the Department of Energy (DOE), Basic Energy Sciences. This provided partial funding for the invited speakers.

The symposium was quite well attended with typically 25-40 people present and a number of useful discussions took place between people using quite different techniques. From our perspective the Symposium was very successful and we anticipate a second symposium on this topic in two years.

Symposium HH: Quantitative Characterization of Nanostructured Materials

April 14 - 16, 2009

Chairs

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* Invited paper

SESSION HH1: Spatially Resolved Techniques I
Chair: Igor Levin
Tuesday Morning, April 14, 2009
Room 3009 (Moscone West)

8:30 AM *HH1.1
STM Measurements of Metallic and Molecular Nanostructures on Metallic Surfaces. <u>Karina Morgenstern</u>, Institute for Solid State Physics, Leibniz University of Hannover, Hannover, Germany.

Scanning tunnelling microscopy (STM) measures the local density of states of a conducting sample with sub-atomic precision in real space. The interpretation of STM images is not always straightforward because of the superposition of electronic with topographic information. On the other hand this superposition allows determining both, the topology of a surface structure directly and its electronic structure by employing elastic and inelastic scanning tunnelling spectroscopy. In this talk I will present results on metallic Cu islands on Ag(100) and small organic molecules on the (111) faces of Cu and Au, where both the topology of the nanostructures and their electronic signature will be discussed. For the metallic Cu islands we resolve a critical size that determines the diffusion and decay behaviour of these nanostructures. For nitrobenzene on Cu(111) and diclorobenzene on Au (111) we find a local variation of the spectroscopic signature with submolecular resolution.

9:00 AM HH1.2

Quantitative Atomic Resolution Imagining with Scanning Transmission Electron Microscopy <u>James Michael LeBeau</u>[1], Scott D Findlay[2], Leslie J Allen[3] and Susanne Stemmer[1]; [1]Materials Department, University of California, Santa Barbara, California; [2]Institute of Engineering Innovation, The University of Tokyo, Tokyo, 113-8656, Japan; [3]School of Physics, University of Melbourne, Melbourne, Victoria, Australia.

Quantitative imaging at the atomic scale remains an active area of research within the electron microscopy community. For instance, high angle annular dark-field (HAADF) in scanning transmission electron microscopy (STEM) provides atomic resolution and atomic number sensitive imaging of nanostructures. However if quantitative information is to be extracted from HAADF STEM images, then complete understanding of the electron scattering theory is required. Previous studies have reported a mismatch between experimental and simulated image contrast for HAADF STEM. However, these previous studies have been hampered by the lack of an absolute intensity scale. Without an absolute measure of image intensities, two possible explanations for the mismatch become indistinguishable: an overestimated signal at the atom columns or an underestimated background (the intensity between the atom columns). Since simulations provide the image intensities on a scale that is normalized to the incident beam intensity, experimental images must be normalized in the same way. For this study, an FEI Titan 80-300 STEM/TEM was operated at 300 kV and equipped with a scintillator-based ADF detector. We will show that the normalization of HAADF images relative to the incident beam intensity is possible using the annular dark field detector that has an output voltage that is proportional to the incident flux averaged over time (intensity). In addition, we will present a method to ensure that the detector does not saturate when measuring the incident beam intensity and show that the typical ADF detector exhibits highly non-uniform detection efficiency as a function of scattering angle. After ensuring that the detector does not saturate and correcting for non-uniformities of the detector efficiency, we construct normalized intensity images of an SrTiO3 single crystal for regions of different thickness. Electron energy loss spectroscopy (EELS) was used to measure the thickness of each image region, but due to surface contributions was found to be in error. We will discussion how the combination of EELS the absolute HAADF background signal can provide improved estimates of the thickness. The normalized intensity images are then compared directly with Bloch wave and frozen phonon image simulations that incorporate thermal diffuse scattering. Once spatial incoherence of the probe is taken into account for the simulations, almost perfect agreement is found between simulation and experiment.

9:15 AM <u>HH1.3</u>
X-ray Photoelectron Microscopy (X-PEEM) Measurements of Local Conduction Band Changes in Si Nanomembranes Induced by SiGe Quantum Dot Nanostressors. <u>Clark S Ritz</u>[1], Chanan Euaruksakul[4], Feng Chen[2], Rebecca A Metzler[1], Mike Abrecht[3], Narayana Appathurai[3], Pupa Gilbert[1] and Max G Lagally[2,1]; [1]Physics Department, University of Wisconsin, Madison, Madison, Wisconsin; [2]Materials Science and Engineering, University of Wisconsin, Madison, Madison, Wisconsin; [3]Synchrotron Radiation Center, University of Wisconsin, Madison, Madison, Wisconsin; [4]Electrical and Computer Engineering, University of Wisconsin, Madison, Madison, Wisconsin.

It is known that strain affects the carrier mobility in semiconductors by splitting and shift-ing bands, but until recently quantitative measurements have not been possible. The availability of elastically strained Si nanomembranes (SiNMs) [1] and high-resolution x-ray absorption spectroscopy (XAS) recently made such measurements possible [2]. The nanomembranes provide large areas of uniformly strained Si, through elastic strain shar-ing in multilayer Si/SiGe/Si sandwich structures. XAS measurements of the Si 2p to conduction band edge transition in strained SiNMs can be used to determine the strain-induced shifting and splitting of minima in the Si conduction band. The growth of epitaxial SiGe quantum dots (QDs) on free-standing SiNMs creates a need to make such measurements of the band edge shifts on a spatially local scale. It is known that these QDs act as nanostressors, with a high local stress, which should cause local variations in the band structure. Because of elastic interactions between strained QDs and the thin SiNM substrate, highly ordered arrays of QDs are formed. We use the "Spectromicroscope for Photoelectron Imaging of Nanostructures with X rays" (SPHINX) at the University of Wisconsin Synchrotron Radiation Center to measure, with better than 100nm spatial resolution, shifts in transition energies in x-ray absorption spectra of SiNMs that have been locally strained with QD nanostressors. We observe local shifts in the L-edge absorption spectra on the order of 100 meV, of the same magnitude as macro-scopic measurements at the same strain. The results support theory predicting local band shifts in the QD-strained SiNMs. [3] This work was supported by DOE, AFOSR, and NSF. [1] M. M. Roberts et al., Nat. Mater. 5 388-393 (2006). [2] C. Euaruksakul et al., PRL 101 147403 (2008). [3] M.-H. Huang et al., Nat. Mater., submitted

9:30 AM <u>HH1.4</u>
Near Nanometer-Resolution Quantitative STEM-EDS Chemical Mapping of Ultrathin Film Multilayer PLZT Capacitors.
<u>Bruce Tuttle</u>[1], Chad M Parish[1], Geoff Brennecka[1], Luke Brewer[1], Jill Wheeler[1], Jacob Jones[2] and John Ekerdt[3]; [1]Sandia National Laboratories, Albuquerque, New Mexico; [2]University of Florida, Gainesville, Florida; [3]University of Texas at Austin, Austin, Texas.

Quantitative analysis of nanometer-scale chemical inhomogeneities has led to the development of lead zirconate titanate (PLZT) ultrathin film multilayer capacitors that have the highest known extended temperature range (-55oC to 125oC) areal capacitance densities reported to date. These advanced multilayer ultrathin film nanostructures were developed to meet areal capacitance requirements for next generation medical electronics, miniaturized sensor devices and energy storage components. In order to achieve this technical break through, it was necessary to quantitatively understand the nanometer-scale structure and chemistry of these materials. Traditional chemical nanoanalysis techniques, such as point or line analyses in electron microscopy or surface-analysis depth profiling, are poorly suited to resolve these fine-scale chemical inhomogeneities. Assisted by computational multivariate statistical analysis, we have developed an X-ray spectroscopy technique in scanning transmission electron microscopy to map cation distributions at the sub-10-nm level in PLZT. We will summarize the developed technique and discuss artifacts and technical challenges as well the many benefits. Results obtained with this technique indicate that significant Zr/Ti segregation occurs in the growth direction for some ultrathin-film PLZT compositions and is nearly absent in others. It has

been determined that this nanoscale inhomogeneity can have a significant impact on both piezoelectric and dielectric properties. We have also quantified La segregation at perovskite - fluorite interfaces during perovskite growth stages. La segregation was less significant than Zr/Ti segregation for our ultrathin film multilayer capacitors. Optimization of single layer ultrathin films and multilayer capacitor fabrication was significantly aided by the analyses of the electrode/dielectric interface(s) at the nanoscale to evaluate low temperature interactions of ultrathin film PLZT with underlying Pt and ZrB2 electrode technologies. Techniques were developed to fabricate ultrathin film lead lanthanum zirconate titanate (PLZT) dielectric layers less than 50 nm thick using chemical solution deposition (CSD) techniques. PLZT ultrathin films 40 nm thick exhibited dielectric constants greater than 1000 and large maximum polarization values exceeding 40 µC/cm2. Since areal capacitance density - a primary metric for our applications - increases as dielectric layer thickness decreases, the thinnest dielectric thickness values possible with our technology were determined. Functional single layer PLZT ultrathin films of 9 nm thickness have been fabricated using our CSD procedure. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

9:45 AM HH1.5
Advanced TEM Characterization for Catalyst Nanoparticles Using Local Adaptive Threshold (LAT) Image Processing.
Petra Bele[1] and Ulrich Stimming[1,2]; [1]Department of Physics E19, Technical University Munich TUM, Garching, Germany; [2]Division 1, The Bavarian Center for Applied Energy Research ZAE, Garching, Germany.

Metallic and non-metallic nanoparticles, usually supported on non-metallic substrates have attracted much interest concerning their application in the field of electrocatalysis. To determine a catalyst system by means of detailed information about size, morphology, structure and composition (alloys or core-shell) of nanoparticles and their associated electrocatalytic activity, transmission electron microscopy (TEM) is the state of the art method. For a thorough structural characterization of a catalyst system, represented by small nanoparticles on a matrix, we have to deal with the obstacles due to image detection and image processing; in case of the image detection with: i. a variation of image contrast due to local thickness changes of the support material, ii. intensity variation of similar nanoparticles based on diffraction contrast, iii. a weak signal-to noise-ratio due to the difficulty to distinguish particles in the sub-nanometer scale from the matrix, and iv. an overlapping of different particles when imaged in projection. In order to overcome these problems, computer image processing methods offer a major advantage in the data evaluation process. However, computer-assisted analyses of TEM images dealing with nanoscaled or even sub-nm particles have their own difficulties arising from the applied image processing routines itself. Therefore, a function is needed to obtain the image segmentation, which involves the classification of each image pixel to one of the image parts, either object or background. To strive for the most objective results we introduce an advanced computerized image processing routine to evaluate particle size and size distribution. The key for the final determination of the particle diameter is to use the so-called local adaptive thresholding (LAT) instead of the standard global threshold routine before particle picking. By using just a global threshold, one typically has to deal with loosing too much of the desired region or getting too many extraneous background pixels resulting in an under- or overestimation of the desired region. In addition, illumination changes across the image occur causing brighter and darker parts not correlated to the real objects in the image. LAT typically takes a grey-scale image as input and outputs a binary image representing the segmentation assuming that smaller sub-image regions are more likely to have approximately uniform illumination compared to the complete image. Applying the LAT is the key for an exact determination, even for particles in the sub-nanometer scale, leading to a higher degree of accuracy concerning the complete data analysis process. This is demonstrated by a study using different catalysts on different support materials combining TEM data with results received from other electrochemical experiments.

10:30 AM HH1.6
Quantitative Scanning Transmission Electron Microscopy for the Measurement of Thicknesses and Volumes of Individual Nanoparticles. Helge Heinrich[1,2] and Biao Yuan[1]; [1]AMPAC, University of Central Florida, Orlando, Florida; [2]Physics Department, University of Central Florida, Orlando, Florida.

In Scanning Transmission Electron Microscopy (STEM) the High-Angle Annular Dark-Field (HAADF) signal increases with atomic number and sample thickness, while dynamical scattering effects and sample orientation have little influence on the contrast. The sensitivity of the HAADF detector for a FEI F30 transmission electron microscope has been calibrated. Additionally, a nearly linear relationship of the HAADF-signal with the incident electron current is confirmed. Cross sections of multilayered samples for contrast calibration were obtained by focused ion-beam (FIB) preparation. These cross sections contained several layers with known composition. A database with nine pure elements and seven compounds has been compiled so far, containing experimental data on the fraction of electrons scattered onto the HAADF detector for each nanometer of sample thickness. Furthermore, the HAADF-scattering cross sections for several elements have been determined using the FIB samples for calibration. Contrast simulations are based on the multislice formalism and confirm the differences in HAADF-scattering contrast for the elements and compounds. TEM offers high lateral resolution, but contains little or no information on the thickness of samples. Thickness maps in energy-filtered transmission electron microscopy, convergent-beam electron diffraction and tilt series are so far the only methods to determine thicknesses of particles in a transmission electron microscope. We show that the calibrated HAADF contrast can be used to determine the thicknesses of individual nanoparticles deposited on carbon films. With this information the volumes of these nanoparticles were determined. The HAADF-STEM contrast was used to obtain thickness and volume information for FeAu, Pt, Au, and Ag nanoparticles.

10:45 AM HH1.7
Abstract Withdrawn

11:00 AM <u>HH1.8</u>
TEM Lattice Imaging with FFT Analysis of InGaN QWs in GaN Nanowires. <u>Roy H. Geiss</u>, Kris A Bertness, Alexana Roshko and David T Read; NIST, Boulder, Colorado.

Analysis of fast Fourier transforms (FFTs) of lattice images obtained using transmission electron microscope (TEM) imaging of GaN nanowires containing InGaN quantum wells (QWs) showed a 4 to 10% increase of the c-axis lattice parameter values and essentially no change in the a-axis values. Sub-pixel analysis of the FFTs provided picometer (pm) precision in the measurements. Further, multi-colored lattice images made by constructing multiple inverse FFTs (IFFTs) from selected values in the FFT covering the range of measured c-axis parameters provided a clear representation of the variations in the c-axis lattice. The nanowires containing the QWs were grown by molecular beam epitaxy (MBE) using elemental Ga and In and an RF-plasma N2 source on heated Si(111) substrates. Individual nanowires were collected onto holey carbon grids by dragging the grids across the substrate. These nanowires, which are dislocation-free single crystals with a wurtzite structure, grew in the <0001>. They were approximately 1000 nm long and 60 to 130 nm wide and had hexagonal cross-sections. The In concentration in the QWs ranged from 12 to 15% as determined by a standardless analysis using energy dispersive spectroscopy (EDS). The magnitude of the changes in the c-axis values exceeds values that might be expected considering this In concentration using a linear Vegards law for GaN - InN. Therefore at least some of the observed expansion of the c-axis in the QWs is thought to be associated with strain in the <0001>. The FFT analysis showed that the c-axis lattice expansion tracked with the specimen width, being larger by a factor of ~3% for nanowires having two times the width. Convergent beam electron diffraction (CBED) in the TEM was also used, and showed similar changes in <0001> direction in the QW. The same specimens used for the TEM study were analyzed using a newly developed transmission electron diffraction technique in the scanning microscope (SEM). Strain analysis, incorporating electron backscattered diffraction (EBSD) patterns in this completely new and different venue, confirmed the TEM FFT observations. Finally, finite element modeling (FEM), considering elastic behavior, was used to examine the consistency of the observed behavior with expectations from linear elasticity.

11:15 AM <u>HH1.9</u>
Chemical Nano-tomography of Self-assembled Ge-Si:Si(001) Islands from Quantitative High Resolution Transmission Electron Microscopy. <u>Luciano Andrey Montoro</u>[1], Marina S Leite[1], Daniel Biggemann[1], Fellipe G Peternella[1], Joost K Batenburg[3], Gilberto Medeiros-Ribeiro[1,2] and Antonio J Ramirez[1]; [1]Laboratório de Microscopia Eletrônica, Laboratório Nacional de Luz Síncrotron, Campinas, Brazil; [2]Hewlett-Packard Laboratories, Palo Alto, California; [3]University of Antwerp, Wilrijk, Belgium.

The knowledge of composition and strain distribution with atomic resolution are fundamental steps for the understanding of the chemical and electronic properties of nanostructures. Applications of nanostructured semiconductors in electronic and optoelectronic require a precise knowledge of these features. However, an evaluation of the quantitative 3D chemical distribution on such nanostructures is a major challenge. In this work is presented an advanced methodology for a 3D quantitative chemical mapping based on a quantitative TEM technique. This methodology is applied to GexSi1-x islands grown on Si (001). This material has emerged as the model system for the study of self-assembled nanocrystals, due to explore the conventional Si technology and involve only two miscible elements. In these self-assembled semiconductor islands the chemical composition is a key factor, which determines their size, stability and physical properties. Over the past, many studies considered the islands to have a constant and uniform composition over time. However, recently have been shown that its composition is not only different from the nominally deposited material, but is also non-uniform as a result of the interdiffusion process explained from interplay between thermodynamic, and kinetic effects. The procedure involves the use of geometric phase analysis (GPA) to measure displacement fields in high resolution transmission electron microscopy (HRTEM) images. The GPA method is a powerful tool to quantify small periodicity changes in the HRTEM images, allowing the determination of lattice distortions. From the distortion maps and applying a mathematical algorithm which takes into account Vegard's Law and classical elastic theory (Poisson ratio) it is possible to obtain 2D chemical maps with atomic column resolution. To improve the accuracy of these quantitative chemical maps, the HRTEM images were obtained from an exit-plane wave-function reconstruction method, obtaining aberrations-free images. The samples were grown by CVD method and the specimens for HRTEM analyses were prepared by cross-section method in the [100] and [110] zone axis. A JEM-3010 URP with LaB6 electron gun was used at 300 kV. Thus, 2D projected chemical maps with atomic-column resolution were obtained from representative islands viewed from two crystallographic directions [110] and [100]. Systematic differences in these projected chemical maps reveals non-cylindrically symmetric 3D chemical features. By using the two projected maps, and due to the structural symmetry of the islands, one can infer the 3D chemical distribution in a self-consistent fashion. A mathematical algorithm was used to iteratively reconstruct the 3D chemical distribution, revealing a four-fold symmetry chemical arrangement within these nanostructures. Therefore, the proposed methodology emerges as a chemical nano-tomography technique that can be especially applied to epitaxially grown nano-structured materials.

11:30 AM <u>HH1.10</u>
Characterization of the NaCl Suzuki Nanoprecipitate Structure by Scanning Force Microscopy. <u>Adam S. Foster</u>[1], Clemens Barth[2] and Claude Henry[2]; [1]Laboratory of Physics, Helsinki University of Technology, Helsinki, Finland; [2]CRMCN-CNRS, Marseilles, France.

Due to their insulating character, the (001) surfaces of bulk alkali halide crystals are emerging as important substrates in many nanosystems. Particular focuses are supported metal nanoclusters for the study of catalytic properties and the adsorption of molecules to the surface for applications in nanoelectronics. For simultaneous characterization of both the substrate and nano-object at the atomic scale, Scanning Force Microscopy (SFM) remains the tool of choice, but on the highly symmetric alkali halide surfaces, unambiguous interpretation of contrast is difficult. Possible solutions, such as using force spectroscopy, are extremely

challenging both experimentally and theoretically, and do not offer a routine approach to the problem. It is clear that a much more desirable setup would provide interpretation directly from images alone. Recently, NaCl crystals were doped with divalent impurity cations as part of a combined SFM and Kelvin probe microscopy study [1]. Above a certain divalent impurity content, the doped NaCl system creates precipitates in their well-known Suzuki phase [2] on the surface. The precipitates are embedded in the NaCl (001) matrix, so that two different types of surfaces regions, which are well separated, can be found. The atomic unit cell of the Suzuki phase is twice as large as the one of NaCl(001) and is composed of three different ions including Na vacancies. In this work we combine SFM experiments with ab initio and atomistic simulations to show quantitatively that all ions in the Suzuki structure (NaCl:Mg2+ or NaCl:Cd2+) can be unambiguously identified in images with atomic resolution, independently of the tip's polarity and the chemical nature of the divalent impurity ions. We explore in detail the dependence of contrast on the tip-surface distance dependence and the role of atomic displacements in observed features. Our results demonstrate that doping NaCl crystals with divalent impurity cations nanostructures the (001) surfaces with Suzuki precipitates, offering templates for adsorption and growth. The resulting ease of interpretation of atomically resolved SFM images, means that the contrast formation is also expected to be much more accessible for supported nano-objects. [1] C. Barth and C.R. Henry, Phys. Rev. Lett. 100, 096101 (2008) [2] K. Suzuki, J. Phys. Soc. Jpn. 10, 794 (1955) and 16, 67 (1961)

11:45 AM HH1.11
Combination of Transmission Electron Microscopy and Fluorescence Spectroscopy of Single Semiconductor Nanocrystals. Sebastian Jander, Andreas Kornowski and Horst Weller; Institute of Physical Chemistry, University of Hamburg, Hamburg, Germany.

Due to the manifold application of semiconductor nanocrystals, like biolabeling and optoelectronic devices, their fluorescence properties are of great interest. Especially on the single particle level quantum dots (QDs) show outstanding optical behavior (e.g. blinking, spectral diffusion), that helps to understand their electronic structure. Since small changes in size, orientation and structure of nanocrystals lead to large changes in their optical properties a comparison of both attributes is essential. We present a method to correlate fluorescence and structural properties of single semiconductor nanocrystals. To investigate the same particle in a confocal laser scanning microscope (CLSM) and a high resolution transmission electron microscope (TEM) different substrates were used. We found that polyvinyl formal covered copper grids and ultrathin silicon nitride membranes can be used to combine both methods. For combined investigations a highly diluted CdSe/CdS/ZnS quantum dot solution was spin coated on the substrate whereas small silicon dioxide spheres were applied to localize the single nanocrystal in TEM and CLSM. Time traces and emission spectra of a single quantum dot were measured. A following TEM correlation brought forward proof that the measured fluorescence originates from a single isolated nanocrystal.

SESSION HH2: Spatially Resolved Techniques II
Chair: Frank Bridges
Tuesday Afternoon, April 14, 2009
Room 3009 (Moscone West)

1:30 PM *HH2.1
SPM-based Analysis of Surface Nanostructures. Ilan Goldfarb, Gili Cohen-Taguri, Shirley Manor, Evgeny Roizin, Mario Levinshtein, Ori Sinkevich and Arie Ruzin; Faculty of Engineering, Tel Aviv University, Ramat Aviv, Israel.

Surface nanostructures are fascinating, because by reducing the crystal size its properties shift from their balk values to some new, quantum-confined state, characteristic of so-created artificial material. Scanning tunnelling microscopy (STM) is ideally suited to characterize such nanostructures, due its supreme lateral atomic resolution and unprecedented vertical sensitivity, which are useful for identification of nanocrystal structure and geometric shape, and its ability to probe surface local density of states (LDOS) using scanning tunnelling spectroscopy (STS), useful for measuring electron confinement in quantum well, wire, and dot nanostructures. In other words, in-plane and out-of-plane measurement of angles and interatomic spacings may occasionally suffice to identify a particular surface phase or structure, and its orientation relations with the substrate and other features of interest, by the ways of classical crystallography (even in the presence of surface relaxations and reconstructions, which may complicate the process of identification). If a quantum nanostructure is formed, characteristic dependence of its electronic structure on physical dimensions can be detected by STS. In semiconductors, electronic contribution to the contrast might be significant even in the absence of quantum confinement, in which case bias-dependent imaging, with or without the STS, must be used to distinguish between the two. In such cases, unambiguous structure identification by STM alone may be difficult without the aid of theoretical modelling, where STM contrast and density of states (DOS) of the suspect structure are iteratively fitted to the experimentally observed ones until a reasonable match is obtained. The problem is even more complex when chemical bonds between chemically distinct species are involved, since STM does not normally provide explicit chemical information. In such cases modelling, or additional experimental techniques, must be used to complement the STM/STS results. Conventional methods, such as diffraction or electron spectroscopies, while useful for obtaining information averaged over relatively large portion of the surface, such as mean surface lattice constant, orientation, composition, etc., cannot provide localized information from individual regions and nanostructures. That is why local probes, such as various derivatives of scanning tunnelling and force microscopy (electric or magnetic force microscopy, etc.) are becoming progressively important in characterization of nanostructured materials surfaces. In this talk, the above characterization methods and combinations will be exemplified by various test cases, such as the initial stages of homoepitaxial and heteroepitaxial semiconductor growth (Si/Si, Ge/Si), metals on elemental (Ti/Si, Co/Si, Fe/Si) and compound (In/CZT) semiconductors, and self-organized nanocrystals.

2:00 PM HH2.2
Structure of Cleaved (001) USb2 Single Crystal Surface. Shao-Ping Chen[1], Marilyn Hawley[2], Phil B. Van Stockum[3], Hari C

Manoharan[3] and Eric D Bauer[4]; [1]Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico; [2]Materials Science and Technology Division, Los Alamos National Laboratory, Los Alamos, New Mexico; [3]Department of Physics and Stanford Institute for Materials and Energy Sciences, Stanford University, Stanford, California; [4]Materials Physics and Application Division, Los Alamos National Laboratory, Los Alamos, New Mexico.

We have achieved what we believe to be the first atomic resolution STM images for a uranium compound taken at room temperature. The a, b, and c lattice parameters in the images confirm that the USb2 crystals cleave on the (001) basal plane as expected. The a and b dimensions were equal, with the atoms arranged in a cubic pattern. Our calculations indicate a symmetric cut between Sb planes to be the most favorable cleavage plane and U atoms to be responsible for most of the DOS measured by STM. Some strange features observed in the STM will be discussed in conjunction with ab initio calculations.

2:15 PM HH2.3
Hybrid Tomography of Nanostructures in the Electron Microscope. Zineb Saghi, T. Gnanavel, Xiaojing Xu and Guenter Moebus; Engineering Materials, University of Sheffield, Sheffield, United Kingdom.

The capability of electron tomography in the TEM for the 3D reconstruction of nanostructures has never been limited by the TEM resolution. This is different for X-ray nanotomography where the underlying x-ray microscope resolution is closer to the achievable tomographic resolution. The reasons for a factor 10 between TEM resolution and TEM-tomogram resolution is linked to: - Suppression of coherent scattering (dark patches in bright-field TEM images due to Bragg reflection excitation), requires incoherent imaging modes, e.g. EFTEM or EDX mapping. Their resolution is inferior to coherent BF-TEM. The additional benefit is spectroscopic tomographic information. - Maximum TEM resolution in HREM can extract an object support only, as the lack proportionality to thickness prevents it for computerised tomographic backprojection. In this case geometric tomography [1] has been demonstrated to reveal the shape-morphology of nanostructures [2] subject to an axial convexity constraint. We present a theoretical concept of combining (e.g. by logical OR or other operators) two results of two tomography experiments using different imaging modes or processing techniques, such as to achieve a "hybrid" tomogram, which comprises: Firstly: A high-definition 3D contour (surface morphology) exploiting full TEM resolution, and Secondly: a tomogram with extra internal information, e.g. chemistry or crystallography. Three experiments show how to usefully combine a pair of tomography disciplines into one hybrid tomogram: (i) Combination of chemical mapping and geometric BF tomography leads to a 3D chemical map with sharper contours than achievable by chemical tomography alone [3]. (ii) Combination of geometric tomography and HREM-lattice backprojection leads to a sharply defined contour combined with the relative grain orientation relationships upon incorporating the concept of lattice goniometry [4]. This technique is not to be confused with atomic resolution tomography requiring resolved atoms in all tilt directions (as simulated in e.g. [5,6]). (iii) Combination of geometric tomography with tomographic nanofabrication [7] allows manufacturing and reconstruction of nanostructures within one TEM-session using identical tilt sequences. Highlights of the recent published work will be complemented by fresh experimental results. [1] R.J. Gardner 1995 Geometric Tomography (New York:Plenum Press) [2] Z. Saghi, X.J. Xu and G. Möbus 2008 J. Microscopy 232 186 [3] Z. Saghi, X. Xu, Y. Peng, B. Inkson, G. Möbus 2007 Appl. Phys. Lett 91 , 251906 [4] W. Qin, P. Fraundorf 2003 Ultramicr. 94 245 [5] G. Möbus, R.D. Doole and B.J. Inkson. 2003 Mat.Res.Soc.Symp.Proc., 738, G1.2, 15-20 [6] J.R. Jinschek, et al. 2008 Ultramicr. 108 589 [7] Z. Saghi, et al. 2008 Appl. Phys. Lett. 93 153102

2:30 PM HH2.4
On the use of Analytical Transmission Electron Microscopy to Discern the Role of Microstructure in Influencing the Physical Mechanisms of Fatigue and Wear in Micron-scale Polysilicon. Daan Hein Alsem[1,2], Eric A Stach[3] and Robert O Ritchie[4]; [1]Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California; [2]National Center for Electron Microscopy, Lawrence Berkeley National Laboratory, Berkeley, California; [3]School of Materials Engineering and Birck Nanotechnology Center, Purdue University, West Lafayette, Indiana; [4]Department of Materials Science and Engineering, University of California at Berkeley, Berkeley, California.

Adhesion, wear and fatigue are major issues for the reliability of silicon micron-scale structures, i.e., in microelectromechanical systems (MEMS). The large surface-to-volume ratios of components in these devices can cause the mechanical properties and governing failure mechanisms to be quite different from those commonly seen in macroscale structures. Here we focus on the cyclic fatigue and wear behavior of micron-scale polycrystalline silicon in ambient air using two on-chip MEMS testing devices and seek to explain the observed behavior in terms of the salient physical mechanisms affecting performance failure using a combination of high-voltage (HV), energy filtered (EF) and energy dispersive x-ray analysis (EDS) transmission electron microscopy (TEM). Using cross sectional site-specific silicon-oxide measurements, fatigue is shown to occur via moisture-assisted sub-critical cracking within a cyclic stress-assisted thickened nano-scale oxide layer (up to tens 10s of nm) until the crack reaches a critical size to cause catastrophic device failure. For contacting sidewall surfaces wear is shown to involve a short adhesive wear regime, where the post-release oxide (~3.5 nm) is worn and the first silicon debris forms, followed by an abrasive wear regime, where 50-100 nm silicon debris particles are created by fracture through the silicon grains (~435 nm). These particles subsequently oxidize while plowing by this debris leads to abrasive grooves associated with local cracking rather than plastic deformation. In situ TEM experiments are used to confirm the role of these physical mechanisms.

2:45 PM HH2.5
On the Measurement of Porosity using Valence Electron Energy-loss Spectroscopy. Nan Jiang, Physics, Arizona State University, Tempe, Arizona.

Nanoporous materials have very unique properties that the corresponding bulk materials may not have, due to their high surface-

to-volume ratio. Over the years, porous materials continue to attract a great deal of attention because of many promising applications ranging from sonic and thermal insulation or lightweight structural materials to energy production and storage, catalysis, sensors and biological applications. One of important parameters characterizing porous materials is porosity, which is generally the ratio of void volume to solid volume. For large and open voids, the porosity can be accurately measured by using chemical or physical gas adsorption and Mercury Intrusion Porosimetry as well. However, for small (e.g. smaller than a few nanometer in diameter) or closed pores, these methods may not always work. To determine porosity of nanoporous materials, one can take the advantage of transmission electron microscopy, which can directly image porous structure with very high spatial resolution (~ 0.5Å). However, TEM images are projection of objects along beam direction, and thus the individual nanopores may not be easily distinguished due to the overlap. This shortage may be overcome by using the 3-dimention tomography technique, which is however time consuming and difficult to operate experimentally. Here we introduce a new method to determine porosity of nanoporous materials, based on valence electron energy-loss spectroscopy (EELS). The method is based on effective medium dielectric theory. In inhomogeneous materials consisting of a fine scale mixture of different dielectric phases, the dielectric response is distinctively different than in the bulk materials, and can be replaced by effective medium response function $\varepsilon_{eff}(\omega)$. In the case of small voids embedded in dielectric A, an effective excitation function can be easily written down by averaging over bulk loss function $Im(-1/\varepsilon_A)$ and interface loss function $Im(-3/(1+2\varepsilon_A))$: $Im(-1/\varepsilon_{eff})=A \times Im(-1/\varepsilon_A)+B \times Im(-3/(1+2\varepsilon_A))$ The coefficients A and B are proportional to the fraction of the fast electron trajectory in voids and bulk material A. The experimental valence EESL spectrum in nanoporous materials can be fitted using above equation. The porosity can thus be deduced from fitting parameters A and B. This method has been applied to nanoporous MgO. The bulk plasmon shifts are observed in nanoporous MgO and the shift energy depend on the porosity. We successfully reproduced the experimental spectra by the effective medium dielectric theory and porosities were calculated using the fitting parameters. The results are consistent with measurements by other method.

3:30 PM <u>HH2.6</u>
Nanotomographic Mapping of Pt in Ni1-xPtx/Si(100) Thin Films on an Atomic Scale Using Three-dimensional Local-electrode Atom-probe (LEAP®) Tomography. <u>Praneet Adusumilli</u>[1], Conal E Murray[2], Lincoln J Lauhon[1] and David N Seidman[1]; [1]Materials Science and Engineering, Northwestern University, Evanston, Illinois; [2]IBM Thomas J. Watson Research Center, Yorktown Heights, New York.

As we move from 45 nm technology node today to 32 nm and then to 22 nm nodes, the variability in MOSFET characteristics, primarily due to the discrete distribution of dopant atoms, is a major challenge facing the semiconductor industry. As feature sizes decrease, producing abrupt interfaces and very specific dopant and composition profiles will be of paramount importance. Three-dimensional (3-D) laser-assisted atom-probe tomography, is capable of 3-D composition profiling with single-atom sensitivity and sub-nanometer resolution, and is ideally suited for metrology at this length scale. Nanotomography, using a 3-D local-electrode atom-probe (LEAP®) tomograph, also enables us to study buried interfaces in 3-D in great detail; an ability that was hitherto unavailable. Integration of NiSi source/drain contacts in CMOS field effect transistors is challenging due to thermal degradation of this low-resistivity material via agglomeration and phase changes at elevated temperatures. Addition of transition metals, Pt or Pd, enhances the thermal stability and increases the thermal window available for applications. 3-D LEAP tomography is used in this study to map the 3-D distribution of Pt in Ni monosilicide thin films to obtain insights into the role played by Pt in phase stabilization. A solid-solution Ni0.95Pt0.05 film on a Si (100) substrate was subjected to a conventional rapid thermal anneal to form the monosilicide phase. 3-D LEAP tomography samples were prepared using the lift-out technique. Pt was found to segregate at grain boundaries (GBs) of the NiSi phase as well as at the silicide/silicon heterophase interface. A decrease of the interfacial Gibbs free energy due to GB segregation and interfacial segregation might be responsible for the stabilization of monosilicide to elevated temperatures. The silicide/Si interface is also reconstructed in 3-D on an atomic scale and its chemical roughness evaluated.

3:45 PM <u>HH2.7</u>
Atomic-resolution and Three-dimensional Imaging of Bio-inspired and Biogenic Nanostructures Inside Polymer-incorporated Calcite Crystals. <u>Huolin L. Xin</u>[1], Hanying Li[2], Lara A Estroff[2] and David A Muller[3]; [1]Department of Physics, Cornell University, Ithaca, New York; [2]Department of Materials Science and Engineering, Cornell University, Ithaca, New York; [3]School of Applied and Engineering Physics, Cornell University, Ithaca, New York.

Biogenic calcite (CaCO3) crystals, such as sea urchin spines, are known to incorporate biomacromolecules while still preserving their single crystallinity. Guided by the natural structures, we constructed porous structures inside of single crystals by incorporation of polymer networks. Here we report atomic resolution and three-dimensional imaging comparing the calcitic prisms from mollusk shells with bio-inspired nanostructures inside synthetic calcite crystals grown in agarose hydrogel using annular dark field scanning transmission electron microscopy (ADF-STEM). Three-dimensional (3-D) images of the incorporated polymer network in calcite crystals were reconstructed by ADF-STEM tilt-series tomography with ~1-3nm resolution. While the host calcite was confirmed to be single crystal by both selected area electron diffraction and atomic-resolution ADF-STEM images, with 3-D tomographic investigations, the internal polymer network of gel-grown crystals is found to be disordered at a scale of tens of nanometers. Atomic-resolution ADF-STEM imaging also provided information on the atomic arrangement at the interface between ~10nm diameter polymer fibers and calcite. In gel-grown crystals, termination of the high-energy facets, such as {012}, on agarose hydragel fibers was observed. This suggests kinetic limited growth: concave growth fronts engulf the polymer fibers instead of normal convex growth fronts. Direct imaging of biogenic and synthetic calcite using STEM was previously considered infeasible due to the focused dose of electrons incident on the sample and the high radiation sensitivity of CaCO3. However, using a variety of imaging strategies a reliable three-dimensional reconstruction of the polymer network in gel-grown calcite single crystal and in biogenic prisms from a focused ion beam (FIB) lift-out preparation were obtained. While we were able to successfully characterize these systems at atomic resolution by STEM, we found that TEM imaging—typically thought to render

less damage than STEM—introduces unexpected poly-crystalline artifacts in the center of the illumination area in our investigations.

4:00 PM HH2.8
3D Quantitative Characterization of Local Structure and Properties of Contact Materials Alexandra Velichko, Christian Selzner and Frank Muecklich; Materials Science, Functional Materials, University of Saarland, Saarbrücken, Germany.

The characterization of spatial distribution of different phases in the material provides understanding of structural influence on the properties and allows to make physically well-grounded correlations. The FIB/SEM nanotomography opens new possibilities for the target microstructure characterization on the scales from 10 nm to 100 µm. It is based on the automatic serial sectioning by the focused ion beam (FIB). Scanning electron microscope in high resolution mode can be used for the imaging of the nanostructural materials. Additionally energy dispersive spectroscopy (EDS) and electron back scattered diffraction (EBSD) contrast mechanisms provide the information about chemical composition, crystal structure, texture, stress, and strain of the different phases. After imaging, a detailed 3D image analysis enables the comprehensive quantitative evaluation of local microstructure. The possibilities of these techniques will be presented on the example of silver-composite contact materials which were analysed using FIB nanotomography before and after exposure to plasma discharge. Significant changes in the spatial distribution of the oxide particles within the switched zone induce among other effects the changes in the local electric and thermal properties. These cause eventually the failure of the contact material. Advanced methods of image analysis allow characterization of inhomogeneous distribution of oxide particles in silver contact materials. Quantitative parameters characterizing the agglomeration of oxide inclusions and accumulation of pores can be derived from the results of distance transformations and morphological operations. The additional consideration of the connectivity allows the quantification of homogeneous and inhomogeneous states with high sensitivity and confidence level. Local thermal and electrical properties were estimated using simulation software on the real tomographic data. The combination of FIB microstructure tomography with modern 3D analysis and simulation techniques provides new prospects for targeted characterization and thus understanding of the microstructure formation and local effect associated with e.g. electro-erosion phenomena. First correlations between 3D microstructure parameters and resulting properties will be discussed in the presentation.

4:15 PM HH2.9
3D Reconstruction at the Nanoscale: Mapping Graphene Waviness. Luca Ortolani[1,2], Florent Houdellier[2], Marc Monthioux[2] and Vittorio Morandi[1]; [1]IMM-Bologna, CNR, Bologna, Italy; [2]CEMES, Toulouse, France.

Soon after the experimental evidence of its existence[1], graphene has increasingly attracted interest in the scientific community due to the extraordinary electronic, mechanical and optical properties. Graphene is a two-dimensional (2D) crystal of carbon atoms arranged in a honeycomb lattice, where its exotic properties are tightly bounded to the electronic structure and strongly modified in the presence of local undulations and/or bending in the structure itself[2]. To date, only few experimental results indirectly provide information on the three-dimensional (3D) atomic structure in graphene from the investigation of peaks intensities in electron diffraction patterns[3]. Here we present a novel method to reconstruct the 3D waviness at the nanoscale of 2D crystal (i.e. graphene) from high-resolution transmission electron (HREM) images. Differently from other approaches, such as electron tomography[4], our method requires only one HREM micrograph of a crystal flake and relies on the geometrical analysis of the spatial frequencies composing the image to recover 3D information[5]. An HREM image contains information on the z-projection of the crystal atomic structure, where the arrangement of crystal planes are imaged as interference fringes modulated in space according to interplanar distances. Using flakes simple geometry and low-voltage aberrations-corrected TEM high-resolution, 3D crystal deformation can be directly reconstructed from apparent interplanar distances modifications with nanometer lateral resolution and sub-nm height precision. Results in the reconstruction of the waviness in graphene membranes are presented, along with a discussion of the limits of the present method. 1. Novoselov, K.S. et al., *Two-dimensional atomic crystals*, Proc. Natl. Acad. Sci. USA **102**, 10451-10453 (2005). 2. Geim, A.K. and Novoselov, K.S., *The rise of graphene*, Nature Mat. **6**, 183-191 (2007). 3. Meyer, J.C. et al., *The structure of suspended graphene sheets*, Nature **446**, 60-63 (2007). 4. Midgley, P.A., et al., *STEM Electron Tomography for Nanoscale Material Science*, Microsc Microanal **10**, 148-149 (2004). 5. Hytch, M.J. et al., *Quantitative measurement of displacement and strain fields from HREM micrographs*, Ultramicrosopy **74**, 131-146 (1998).

4:30 PM HH2.10
Nanoscale Chemical Tomography Using 4D STEM/EELS Donovan Nicholas Leonard[1], Konrad Jarausch[2], Paul Thomas[3], Ray Twesten[3] and Christopher Booth[3]; [1]Physics & Astronomy, Appalachian State University, Boone, North Carolina; [2]Hitachi High Technologies America, Inc., Pleasanton, California; [3]Gatan, Inc., Pleasanton, California.

Advances in electron based instrumentation are enabling multi-dimensional data acquisition to explore the unique structure property relationships of nanostructured materials [1-3]. Here we report a technique for directly probing and analyzing a material's three-dimensional (3D) electronic structure. A rotation holder is used to vary specimen orientation and record STEM EELS spectrum images at regular angular intervals (using a Hitachi HD2300A FEG-STEM equipped with a Gatan ENFINA spectrometer). Experimental conditions were optimized to facilitate acquisition rates of over 100 spectra/second and thereby make the acquisition of such large data sets practical. By using a pillar shaped sample, and a rotation holder the electronic properties are sampled with a constant projection thickness and over a complete 180 degree rotation to minimize artifacts. Analysis software was developed to align the four-dimensional (4D) data volume, and extract the spectral properties of interest [5]. By combining energy loss information from such a series of spectrum images it is possible to map not only the microstructure, but also the elemental, physical and chemical state information of a material in three dimensions. Details and limitations of the 4D

STEM-EELS acquisition will be discussed in addition to the options and requirements for analysis of 4D EELS data sets. This technique has been applied to map the 3D properties of a variety of samples and two examples are reported here. 4D STEM/EELS was used to directly probe a W to Si contact from a semiconductor device and a ZnO film with embedded Au nanodots. The 4D data sets were analyzed to map the composition, bonding and phases of the W to Si contact in three dimensions. Providing the chosen EELS signal meets the projection criterion, tomo-graphic reconstruction can be used to obtain a "volumetric" map of the property of interest. The ZnO thin film was specially prepared to allow sampling of the electronic properties over a range of crystallographic orientations using a single axis of rotation. The film was rotated from e-beam parallel to the c-axis to e-beam perpendicular to c-axis, and then back again. Subtle, but systematic changes in low-loss structure were observed as a function of sampling angle, similar to those reported elsewhere [6,7]. These two examples illustrate how the 4D STEM EELS technique can be used to directly probe the electronic structure of complex nanostructures in three dimensions. 1. C. Jeanguillaume and C. Colliex, Ultramicroscopy 28 (1989) p. 252. 2. P.A. Midgley and M Weyland, Ultramicroscopy 96 (2003) p.413. 3. M H. Gass et al., Nano Letters 6 (2006) 376. 4. T. Kamino et al., J. Electron Microscopy 53 (2004) p.583. 5. K. Jarauch, et al., Under review Ultramicroscopy. 6. Juan Wang, et al., Applied Physics Letters 86 (2005) p.201911. 7. Yong Ding, et al., Journal of Electron Microscopy, 54 (2005) p.287.

4:45 PM HH2.11
Abstract Withdrawn

SESSION HH3: Local Structure
Chair: Thomas Proffen
Wednesday Morning, April 15, 2009
Room 3009 (Moscone West)

8:30 AM *HH3.1
Atomic Structure of Nano-Particles. Takeshi Egami[1,2] and Wojtek Dmowski[1]; [1]Mater. Sci./Physics, University of Tennessee, Knoxville, Tennessee; [2]Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Often nano-particles exhibit unique or different properties not just because of the particle size, but the structural modification that small size makes possible. Small angle scattering that determines the particle size thus will not be sufficient in characterizing nano-particles. The PDF technique provides information on both the local structure and the particle size, although the information is averaged over the entire sample. We discuss the structure of nano-particles determined by high-energy x-ray PDF method for hydrated ruthenia (RuO_2) used for super-capacitance and fuel cells, and gold nano-particles that are catalytically active. Judged from diffraction patterns and EXAFS results strongly hydrated ruthenia nano-particles were considered to be amorphous. But the PDF clearly shows that they are nano-crystalline, and local crystal structure is relevant to electron conduction, while water in-between and interface allow proton conduction. Bulk or crystalline gold (Au) is inactive as a catalyst, but nano-crystalline gold particles within a certain range of size are catalytically active for CO oxidization. High-energy in-situ X-ray PDF has shown that the atomic structure of gold particles locally change with temperature, departing from the usual f.c.c. structure and resembling the b.c.c. structure. Even at room temperature a portion of the surface appears to show the transformed structure. We conjecture that the change in the electronic structure due to the atomic structure modification, widening of the d-band in particular that will create holes in the d-band, is responsible for the catalytic activity. The PDF technique is a powerful tool to characterize these local changes in the atomic structure that are relevant to the properties of nano-particles.

9:00 AM *HH3.2
Resolving Complexity of Nanoscale Metal Clusters. Anatoly Frenkel, Physics, Yeshiva University, New York, New York.

Negative thermal expansion (NTE), a peculiar effect reported in 1996 in zirconium tungstate and other framework solids and not expected in fcc metals, was recently observed in alumina-supported Pt nanoparticles. In the smallest particles studied (0.9nm in diameter) the Pt-Pt distance decreased gradually by 0.04 Å over the 500 K range. Such effect was attributed to the charge transfer between the cluster and support. I will review recent experiments using x-ray and electron microscopy techniques that allow to resolve competing interactions between metal and substrate, metal and adsorbate, and between alloying metals (for bimetallics). Experimental (x-ray spectroscopy and electron microscopy) results combined with the first principles, real-time calculations uncover dynamic structure and mobility of supported metal clusters that. This dynamic behavior is the origin of very peculiar electronic and structural effects in these supported clusters that explains their observed anomalies.

9:30 AM HH3.3
Using First Principles Based Simulations to Solve the Nanotructure of a Relaxor Ferroelectric. Benjamin Paul Burton[1], Eric Cockayne[1], Panchapakesan Ganesh[2] and Ronald Cohen[2]; [1]Ceramics Division, NIST, Gaithersburg, Maryland; [2]CIW, Washington DC, District of Columbia.

Molecular dynamics simulations were performed on a first-principles-based effective Hamiltonian for the relaxor ferroelectric system: $Pb(Sc_{1/2}Nb_{1/2})O_3$ (PSN). Temperature-dependent polar ordering was simulated in a nano-ordered (NO) Sc:Nb-configuration with 20 approximately spherical chemically ordered regions (COR) in a percolating random matrix (PRM). The model was used to generate simulated neutron and X-ray diffuse scattering (DS) patterns. In agreement with experiment: 1) in the temperature/pressure range in which the model yields a relaxor-like state, calculated DS patterns for the [110] peak are lozenges with their long dimensions perpendicular to [110], and for the [010] peak are "butterflies" (crossed lozenges); 2) at temperature/pressures above which the model yields a transition to the paralectric phase, the lozenges and butterflies disappear.

The characteristic DS of the model arises from the formation of polar nanoregions (PNR) centered on the COR. It is more challenging to explain the full three-dimensional experimental diffuse scattering pattern, which may require an effective Hamiltonian with more parameters, or a more realistic representation of the chemical ordering. By systematically varying the simulation box configuration, however, we expect the nature of the nanostructure can ultimately be identified. The general idea is an old one, to solve a (nano)-structure: build a model, calculate the scattering (diffraction), vary the model to optimize the fit between experiment and theory. The nanostructural picture that emerges from our simulations is one of PNR that, to first order, are spatially static but orientaionally dynamic. Spatially static because PNR are strongly correlated with COR. Orientationally dynamic because the simulations exhibit PNR/COR in which local-mode displacements are more strongly correlated than in the PRM, whith average orientations that rotate rather freely.

9:45 AM HH3.4

Atomic and Electronic Structure of Graphene-Oxide. <u>K. Andre Mkhoyan</u>[1,2], Alexander Contryman[2], John Silcox[2], Derek Stewart[3], Goki Eda[4], Cecilia Mattevi[4], Steve Miller[4] and Manish Chhowalla[4]; [1]Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota; [2]Applied Physics, Cornell University, Ithaca, New York; [3]Cornell Nanoscale Facility, Cornell University, Ithaca, New York; [4]Materials Science and Engineering, Rutgers University, Piscataway, New Jersey.

The solubility of graphene oxide (GO) sheets, which recently emerged as a new carbon-based nanoscale material, in water allows it to be uniformly deposited in the form of thin films or networks which makes them potentially useful for macroelectronics [1,2]. Graphene oxide is an insulator but controlled oxidation provides tunability of the electronic and mechanical properties including the possibility of accessing zero-band-gap graphene via complete removal of the C-O bonds. The structure of GO is often simplistically assumed to be a graphene sheet bonded to oxygen in the form of carboxyl, hydroxyl or epoxy groups. Here, we elucidate the atomic and electronic structure of GO using composition sensitive annular dark field (ADF) imaging of single and multilayer sheets and electron energy loss spectroscopy (EELS) for measuring the fine structure of the carbon and oxygen K-edges as well as low-loss electronic excitations in a scanning transmission electron microscope (STEM). The results reveal that the GO sheets are rough with an average roughness of 0.6 nm and the structure is predominantly amorphous due to distortions from the high fraction of sp3 C-O bonds. Our results suggest that chemical removal of oxygen, using hydrazine for example, may leave behind a highly distorted reduced graphene oxide sheet which is likely to have substantially lower carrier mobilities than pure graphene, as has been observed in several device studies [2]. Electron energy loss spectroscopy combined with STEM-ADF imaging and AFM-depth profiling shows that graphene oxide films have substantially different density-of-states and resonance electron plasma excitation energy than those in graphene and a-C. It also indicates that oxygen atoms during the oxidation process attach to graphene sites randomly and convert sp2 carbon bonds in graphene to sp3 bonds. While the structural modifications of graphene are dependent on the oxidation level, the results show that a ratio of 1 to 5 oxygen to carbon atoms is sufficient to transform the measured 40% of the carbon bonds into sp3 bonds. As a consequence, the atomic structure of oxidized graphene sheets is highly distorted, becoming a semi-amorphous sheet of solid carbon-oxide with undulations resulting in a surface roughness of about 0.6 nm. These results are also supported by our ab initio calculations. Our results provide new insight into the structure of graphene oxide and indicate that in addition to the removal of oxygen, structural ordering of the remaining graphene sheets is necessary if high mobilities from reduced graphene oxide devices are to be achieved [3]. [1] S. Stankovich et al., Graphene-based composite materials, Nature 442, 282-286 (2006). [2] G. Eda et al., Large-area ultrathin films of reduced graphene oxide as a transparent and flexible electronic material, Nature Nanotechnology 3, 270-274 (2008). [3] K.A. Mkhoyan et al., Atomic and electronic structure of graphene-oxide, (submitted).

10:30 AM *HH3.5

Periodicity and Atomic Ordering in Nanophase Crystals. <u>Valeri Perkov</u>, Physics, CMU, Mt. Pleasant, Michigan.

Evidence is mounting that nanophase crystals do not necessarily adopt the periodic structure of their bulk counterparts or any other structure that may be considered as a stack of well defined unit cells/atomic planes, and that this may affect their properties substantially. We will show how a combination of experimental and computational techniques including total x-ray diffraction, EXAFS, Density Functional Theory, "real-space" Rietveld and reverse Monte Carlo simulations may be employed to determine the atomic ordering in nanophase "crystals" with any degree of structural periodicity with success [1,2,3,4]. References: 1. M. Gateshki et al. "Atomic scale structure of nanocrystalline ZrO2", Phys. Rev. B 71 (2005) 22410. 2. S. Pradhan et al. "Atomic-scale structure of nanosize titania and titanate: particles, wires and tubes", Chem. Mat. 19 (2007) 6180 3. V. Petkov et al. "Periodicity and atomic ordering in nanosized particles of crystals" J. Phys. Chem. C 112 (2008) 8907. 4. V. Petkov et al. "Structural Coherence and Ferroelectricity Decay in Submicron- and Nanosized Perovskites", Phys. Rev. B 78 (2008) 054107.

11:00 AM HH3.6

Crystallographic Characterization of Nanostructured and Amorphous Materials using High-energy X-rays by means of X-ray Diffraction on a Homelab System. <u>Hans te Nijenhuis</u>, Milen Gateshki, Detlef Beckers and Martijn J Fransen; Product Management XRD, PANalytical B.V., Almelo, Netherlands.

Recent interest in the understanding of physical and chemical properties of nanomaterials has increased the need to analyze structures on a local (nano) scale. However, the atomic structures of nanostructured and amorphous materials are not accessible by conventional methods used to study crystalline materials, because of the short ordering range in these materials. One of the most promising techniques to study nanostructures using X-ray diffraction is total scattering pair distribution function (PDF) analysis. The pair distribution function provides information about the probability of finding atoms separated at a certain distance. We have developed the application hf PDF analysis on a standard laboratory system. As X-ray source an X-ray tube with a silver anode was used, delivering characteristic Ag Kα radiation with an energy of 22 keV. The corresponding X-ray wavelength is 0.05564 nm. Samples of different nature -crystalline, nanocrystalline, amorphous solid and even liquid -have been used to test the

applicability of the PDF calculations on the lab measurements. Meaningful results have been achieved, even though the attainable X-ray photon energies are not as high as with synchrotron radiation. The PDF analysis revealed the short range order by determining the existing interatomic distances. The results allowed for comparison with data reported in literature, obtained using high-energy synchrotron radiation.

11:15 AM <u>HH3.7</u>
Defect Study of Graphene and Observation of Mis-orientation using Raman Spectroscopy. <u>Gayathri S Rao</u>, Sarah Mctaggart, Robert E Geer and Ji Ung Lee; College of Nanoscale sciences and engineering, University at Albany, Albany, New York.

Nanoscale metrology (thickness, defectivity) of graphene-based devices is a substantial challenge. The investigation of defects and stacking order is essential for graphene-based device development. Raman spectroscopy has proved to be an appropriate approach in this regard. The defect-induced Raman D and D' peaks give great insight into study of defects and their potential impact on device structures . Toward this end we have carried out a defect study on customized bi-layer and mono layer graphene samples by analyzing the Raman D, D' and 2D bands. Defects were introduced via electron irradiation of customized exfoliates at controlled dose in a Leo 1550 scanning electron microscopy. The evolution of the aforementioned Raman spectra as a function of dose was characterized via microRaman spectroscopy and compared with spectra from the same samples prior to irradiation. The impact of the defects created was visible from the intensity ratios of the D to G Raman bands (ID/IG) before and after defect creation. For bilayer graphene, modification to the 2D band peak-shape and 2D FWHM was also observed as a result of electron irradiation. The peak positions and widths of the 4 fitted 2D Raman band component peaks, explained by the process of double-resonance Raman scattering, was used to infer variations in bilayer-graphene band structure due to the electron irradiation. Preliminary analysis of the 2D1B,2D1A,2D2A and 2D2B Raman peaks from electron-irradiated bilayer graphene exfoliates from ZYH, ZYA, and, presumably, Kish graphite imply that induced defectivity impacts mis-orientation (e.g. from Bernal-type bilayer) and impacts the 2D Raman bands accordingly. These results are discussed and compared to recent Raman analysis of CVD bilayer graphene films.

11:30 AM <u>HH3.8</u>
Synchrotron-Based Analysis of Structural Ordering and its Impact on the Luminescent Properties of Nitride- and Oxynitride-Passivated Silicon Nanoclusters. <u>P. R. J. Wilson</u>[1,2], T. Roschuk[1,2], J. Wojcik[1,2], K. Dunn[1,2], M. Betti[1,2] and P. Mascher[1,2]; [1]Engineering Physics, McMaster University, Hamilton, Ontario, Canada; [2]Centre for Emerging Device Technologies, McMaster University, Hamilton, Ontario, Canada.

Efficient luminescent from silicon can be obtained through quantum confinement effects in the form of silicon nanoclusters (Si-ncs). The Si-ncs are typically formed within Si-based dielectric films and their luminescent properties exhibit complex behaviour largely dependent on the coordination at the Si-nc/dielectric interface and the physical properties of the dielectric matrix. Due to the potential for developing Si-based light sources using such materials systems, research into understanding this behaviour has garnered much interest. X-ray absorption spectroscopy (XAS) experiments have been conducted on a wide range of samples exhibiting different emission properties in an effort to link observed optical phenomena with the structural ordering of the Si-ncs and dielectric host matrix. Samples were prepared through the deposition of silicon-rich nitride (SRSN) and oxynitride (SRSON) thin films using plasma-enhanced chemical vapour deposition (PECVD). Post-deposition processing involved thermal annealing of the samples in quartz tube and rapid thermal annealing furnaces under flowing ambient gas. Samples with different properties were obtained by varying the deposition gas flow rates as well as the annealing time, temperature, and ambient gas used. The luminescent properties of the films were determined with photoluminescence measurements using a 325 nm HeCd laser source. The XAS experiments were performed at the high resolution spherical grating monochromator and variable line spacing plane grating monochromator beamlines at the Canadian Light Source synchrotron facility using photon energies corresponding to the Si, N, and O K-edges and Si L-edges. These experiments provide access to the electronic structure of the films, which can be used to gain quantitative information on the chemical environment and local bonding coordination of the Si-ncs through a spectral deconvolution analysis. For SRSN films, emission appears to originate from both quantum confinement effects and inter-bandgap defect levels. The results from the XAS experiments show structural reordering of both the Si-ncs and host matrix, with evidence of increased phase separation of the clusters occurring at lower temperatures for samples with higher excess silicon concentration. However, the SRSON films only exhibit defect-related emission and the XAS results do not indicate structural changes in the Si-ncs at any annealing temperature while the host oxide and nitride matrices undergo significant reordering. This work has been supported by the Ontario Research and Development Challenge Fund under the auspices of the Ontario Photonics Consortium, by the Centres for Photonics and Materials and Manufacturing, divisions of Ontario Centres of Excellence Inc, and by the Natural Sciences and Engineering Research Council of Canada (NSERC). Part of this work was performed at the Canadian Light Source facility, which is supported by NSERC, CIHR, NRC, and other government agencies.

11:45 AM <u>HH3.9</u>
Transferred to HH3.7

SESSION HH4: Nanoparticles I
Chair: Valeri Petkov
Wednesday Afternoon, April 15, 2009
Room 3009 (Moscone West)

1:30 PM <u>*HH4.1</u>
The Nature and Characterization of Nanoparticles. <u>Rajiv Kohli</u>, NASA Houston Operations, Aerospace Corporation, Houston,

Texas.

Characterization of nanosize particles is essential to understanding their interactions. These particles are of fundamental and practical interest for developing advanced materials and devices and micro and nanostructures. As feature sizes shrink, nanoparticle contamination is also becoming increasingly important to achieve and maintain high product yields. In order to employ appropriate material and product development strategies, or institute preventive assembly and remediation strategies to control nanoparticle contamination, it is essential to understand the nature of nanoparticles and to characterize these particles. Particles in the size range 0.1 nm to 100 nm present unique challenges and opportunities for their imaging and characterization. Critical information for this purpose is the number and size of the particles, their morphology, and their physical and chemical structure. Because of this importance, many advances and new developments have been made in qualitative and quantitative characterization techniques for particles in this size range. For example, aberration-free imaging with sub-Angstrom resolution has been successfully demonstrated in high-resolution transmission electron microscopy. Other developments include combining techniques such as transmission electron microscopy with scanning probe microscopy and other chemically sensitive sensors, in-situ wet transmission electron microscopy, neutron holography, electron and x-ray tomography, three dimensional atom probe imaging, ultrafast microscopy and crystallography, magnetic resonance force microscopy for imaging a single electron spin, sub-micron resolution scanning thermal microscopy, hot electron microcalorimetry, Raman chemical imaging, and high-resolution x-ray crystallography of non-crystalline structures. It is now possible to completely characterize nanoparticles from 0.1 nm to 100 nm size. A brief review of the nature of nanoparticles will be presented and some of these recent developments in characterization techniques will be described.

2:00 PM *HH4.2
Probing Size Effects in Functional Metal Oxide Nanoparticles with the Pair Distribution Function. <u>Katharine Lynn Page</u>, Materials, University of California, Santa Barbara, Santa Barbara, California.

Polar materials play an important role in science and engineering, and efforts to understand, characterize, design and engineer them on the nanoscale are driven, for example, by a continued demand for smaller and more robust ferroelectrics. As in many functional inorganics, the properties of polar materials are intricately tied to their crystal structures. The limited translational periodicity in nanoscale particles, however, renders reciprocal space methods of limited utility for structural studies. The use of neutron and synchrotron X-ray total scattering data and real-space atomic pair distribution function (PDF) methods for quantitative structural investigation of several metal oxide nanoparticle systems will be presented. With sensitivity to particle size over long length scales and local ordering over the first few nanometers, PDF methods are well-suited to contribute a better understanding of how size and structure influence the properties of nanoparticles. For example, a size dependent investigation of the structure of barium titanate nanoparticles reveals increasing bond distortions with decreasing particle size, in contrast to many average structure reports of decreased tetragonality at similar dimensions. The work will demonstrate that combined approaches in reciprocal and real-space often provide unique insight into atomic configurations that influence properties in nanostructured materials.

2:30 PM HH4.3
Abstract Withdrawn

2:45 PM HH4.4
Characterization of InGaN Nanorod-based LEDs by Transmission Electron Microscopy. <u>Robert Colby</u>[1,3], Dmitri N Zakharov[3], Isaac H Wildeson[2,3], David A Ewoldt[1,3], Zhiwen Liang[1,3], R. Edwin Garcia[1,3], Timothy D Sands[1,2,3] and Eric A Stach[1,3]; [1]Materials Engineering, Purdue University, West Lafayette, Indiana; [2]Electrical Engineering, Purdue University, West Lafayette, Indiana; [3]Birck Nanotechnology Center, Purdue University, West Lafayette, Indiana.

The InGaN materials system has been considered as a candidate for efficient green LEDs. The realization of such devices has been limited by several challenges, including the lattice mismatch of InGaN and GaN, and the range of immiscibility of InN and GaN. Poor mismatch between GaN and potential substrates, such as sapphire, also results in a high density of threading dislocations. As a potential solution to these challenges, a porous dielectric mask is fabricated on GaN and used as a filter for further growth. The porous mask screens threading dislocations from the substrate and allows the growth an array of dislocation-free nanorods. The emerging nanorods form hexagonal pyramids that are used as a template for InGaN/p-GaN quantum well structures. Additionally, it should be possible to achieve a high degree of InN incorporation at the vertex of each pyramid. The characterization of these structures by scanning and conventional transmission electron microscopy (TEM) will be presented. Data suggests that these rods emerge from the template dislocation-free, with a shape that depends on growth temperature. However, GaN/InGaN/p-GaN structures include stacking faults, as well as zinc-blende inclusions that can persist for several nanometers. It is believed that these defects are driven by growth kinetics, initiating at the vertex of the initial GaN pyramid and remaining trapped in the final pyramids after growth. Comparisons to thin film quantum wells grown in parallel with the template-grown pyramids suggest that such defects are unique to the pyramidal structure. To determine the origin of these defects, the quantum well pyramid structures are examined using STEM and high resolution TEM between each growth step, and over a range of growth conditions for each layer. Numerical simulation is used to demonstrate correlation of the expected strains and observed defect structures. This material is based on work supported by the Department of Energy under Award No. DE-FC26-06NT42862.

3:30 PM *HH4.5

The Crystal Chemistry of Ferrihydrite. <u>Benjamin Gilbert</u>[1], Dino Spagnoli[2], Glenn A Waychunas[1], Jillian F Banfield[2,1] and R Lee Penn[3]; [1]Earth Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California; [2]Department of Earth & Planetary Sciences, University of California - Berkeley, Berkeley, California; [3]Department of Chemistry, University of Minnesota, Minneapolis, Minnesota.

Numerous environmentally, technologically and biological important materials are found as nanophase minerals that defy routine structural determination despite advances in electron and x-ray based methods. Ferrihydrite, a ferric iron oxyhydroxide, is one of many nanophase minerals that are widespread in nature and play important roles in subsurface biogeochemical cycles. In a recent breakthrough in understanding the structure of this material, Michel et al., Science 316, 1726 (2007), showed that the experimental pair distribution function data from ferrihydrite samples with a range of particle sizes could be modeled to very high accuracy by a single newly proposed crystal phase. However, important discrepancies remain between experimental x-ray powder structure factors and the scattering predicted by the Michel et al. model. We discuss the origin of the alternative views of nanomaterial structure afforded by long- and short-range structural techniques and suggest that depictions of nanoparticle structure based on a single periodic unit cell should be extended to entire nanoparticle models in order to properly capture chemical and structural diversity. We constructed model nanoparticles based on modifications to the Michel et al. structure, employing simple crystal chemistry principles to guide site coordination at interior and exterior surface sites. Molecular dynamics simulations were used to test the integrity of the candidate structures and to introduce realistic structural distortion. By considering evidence from a range of techniques, we conclude that the structure of ferrihydrite is likely to be very close to that proposed by Michel et al., with additional defects and disorder that cannot be represented by a single unit cell.

4:00 PM HH4.6
Properties of 2 Nm-Diameter ErAs Nanoparticles Embedded in GaAs. <u>Michael A. Scarpulla</u>[1,2], Brent C Melot[2], Arthur C Gossard[2] and Kin M Yu[3]; [1]Department of Materials Science & Engineering, University of Utah, Salt Lake City, Utah; [2]Materials Department, University of California Santa Barbara, Santa Barbara, California; [3]Lawrence Berkeley National Laboratory, Berkeley, California.

The similarity in crystal structure and lattice constant between rare earth pnictides such as ErAs and III-V semiconductors such as GaAs and InGaAs allows the heteroepitaxial growth using molecular beam epitaxy (MBE) of films, islands, and spherical nanoparticles having coherent interfaces. This coupled with the semimetallicity of ErAs has enabled multiple applications as varied as THz sources, detectors, and metamaterials, enhanced tunnel junctions, and thermoelectrics.[1] In this work, we investigate the fundamental structural, optical, electronic, and magnetic properties of codeposited films containing 0.4 to 7.8% ErAs in the GaAs matrix. Bulk ErAs takes the rocksalt structure, is a semimetal, displays metamagnetism, and has a 1.6% larger lattice constant than GaAs. In these samples, ErAs spontaneously phase segregates into approximately spherical nanoparticles of remarkably small dimension - only 2 nm or ~4 unit cells in diameter. <p>The extremely small size of these nanoparticles changes some but not all of the bulk properties of ErAs. Ion beam channeling demonstrates that the ErAs nanoparticles maintain the rocksalt structure; yet no ErAs-related reflections in high-resolution X-ray diffraction are seen because of the nanoparticles' extremely small volume. Diffraction peaks are observed for these pseudomorphic films as in the case of random alloy films, however the change in relaxed lattice constant with composition is over twice the prediction of Vegard's law because of the phase segregation. A resonant near-infrared absorption peak is observed in these ErAs nanocomposite films which can be manipulated via MBE growth conditions. This absorption may be caused by surface plasmon resonances or by excitation across a quantum confinement-induced energy gap. Varying the ErAs volume fraction from 0.7 - 4.5% at a fixed growth temperature of 600 C causes the resonance peak energy to vary from 797 - 570 meV. Varying the growth temperature from 500 to 600 C with 3.2% ErAs shifts the absorption peak from 998 to 618 meV.[2] Magnetization measurements indicate that the small volume to surface area ratio of the nanoparticles suppresses the antiferromagnetic ordering resulting in suppression of the spin-flop transition. Some residual spin disorder is still present even below the bulk Neel temperature of ~4 K and above the spin-flop field of ~1 Tesla as demonstrated by a reduced moment per Er in the nanoparticles. [1]M. P. Hanson et al., Journal of Crystal Growth 301, 4 (2007). [2]M. A. Scarpulla et al., Applied Physics Letters 92, 173116 (2008).

4:15 PM HH4.7
EXAFS Study of AC Electroluminescent ZnS:Cu,Cl Bulk and Nano Crystals. <u>Yu Jiang</u>[1], Carley Corrado[2], Chris France[1], Frank Bridges[1], Sue Carter[1] and Jin Zhang[2]; [1]Physics, University of California, Santa Cruz, Santa Cruz, California; [2]Chemistry, University of California, Santa Cruz, Santa Cruz, California.

The AC electroluminescent (EL) ZnS:Cu,Cl phosphors are potential candidates for solid state lighting applications due to low operation voltage and high electric-to-light efficiency. However, in device structure, these materials degrade with time under applied AC fields. Recently, it was found that the degraded spectrum could be partially rejuvenated by low temperature anneals. Since the AC electroluminescence strongly depends on both the presence of CuS precipitates and substitutional Cu ions, a comprehensive understanding of the local structure and chemical environment around the Cu is essential to improve samples' performance. Further it is known that the device lifetime decreases for smaller diameter particles, and some ground materials were also investigated. In this presentation, we show our Extended X-ray Absorption Fine Structure (EXAFS) study on both the ZnS:Cu,Cl bulk samples (20~40 μm) and nano crystalline ZnS:Cu,Cl (~6 nm) with different concentrations. The latter ware synthesized by our collaborators using a standard aqueous co-precipitation method. For bulk Cu doped material, as made, AC EL degraded, and degraded-plus-thermally- rejuvenated samples were measured at various temperatures. Among them, no apparent changes in the local structure about Cu were found. We also measured the T-depend of CuS. For fits of ZnS:Cu,Cl we found that using CuS as a reference EXAFS function provided an excellent fit to the Cu EXAFS data, which indicates that most of the Cu is in the form of CuS. The correlated Debye temperatures for CuS and ZnS:Cu,Cl are similar (430K and 392K). Thus the average strength of the Cu-S bonds in ZnS:Cu,Cl are about the same as in pure CuS. However, when the material was ground, the X-ray

absorption near edge structure (XANES) at the Cu K-edge changed, which is an indication of changes in the Cu local structure. We should the first results for the XANES measurements. Nano samples also show green and blue photoluminescence, which are attributed to Cl- and Cu+ centers. The Cu-blue center is proposed to be formed of two Cu+ ions, one on-site and one in a neighboring interstitial site. No evidence is found for a significant fraction of interstitial Cu+ - any interstitial Cu+ must be less than 5%.

4:30 PM HH4.8
Structural Characterization of GeSn Alloy Nanocrystals Embedded in SiO2. <u>Swanee J Shin</u>[1,2], Julian Guzman[1,2], Chun-Wei Yuan[1,2], Christopher Y Liao[1,2], Peter R Stone[1,2], Oscar D Dubon[1,2], Andrew M Minor[1,2], Masashi Watanabe[2], Joel W Ager[2], Daryl C Chrzan[1,2] and Eugene E. Haller[1,2]; [1]MSE, UC Berkeley, Berkeley, California; [2]Materials Sciences Division, Lawrence Berkeley National Lab, Berkeley, California.

GeSn alloy nanocrystals were formed by implantation of Ge and Sn ions into an amorphous SiO2 matrix and subsequent thermal annealing. High resolution transmission electron microscopy (HRTEM) and scanning transmission electron microscopy (STEM) with a high angle annular dark field (HAADF) detector were used to show that phase segregated bi-lobe nanocrystals were formed. Rapid melting and solidification using a single excimer laser pulse transformed the bi-lobe structure into a homogeneously mixed amorphous structure. Raman spectroscopy was used to monitor the crystalline nature and approximate grain size of the Ge portion of the nanocrystals after each heat treatment, and the Raman spectra were compared with the TEM images. Extended x-ray absorption fine structure (EXAFS) measurements were performed to determine the local atomic configuration of each structure. The coordination numbers and bond lengths were consistent with the TEM results.

4:45 PM HH4.9
Structure Determination of CoPt Nanoparticles: Chemical Ordering and its Effect on Magnetic Properties. <u>Nils Blanc</u>[1], Laurent Bardotti[1], Matthias Hillenkamp[1], Alexandre Tamion[1], Juliette Tuaillon-Combes[1], Veronique Dupuis[1], Florent Tournus[1], Edgar Bonet[2], Helio Tolentino[2], Aline Ramos[2], Maurizio De-Santis[2], Philippe Ohresser[3] and Thierry Epicier[4]; [1]Laboratoire de Physique la Matière Condensée et Nanostructures, CNRS & Université Claude Bernard Lyon 1, Lyon, France; [2]Institut Néel, CNRS & UJF, Grenoble, France; [3]Synchrotron SOLEIL, CNRS, Saint-Aubin, France; [4]Laboratoire MATEIS, CNRS & INSA, Lyon, France.

Due to the extremely high magnetocrystalline anisotropy of the bulk CoPt alloy, crystallized in the L10 chemically ordered phase, CoPt nanoparticles have been widely studied during the last decade, as they represent good candidates for high-density magnetic storage applications. However, the intrinsic magnetic properties of these particles, which are directly linked to their local structure, are very difficult to determine. Investigating the magnetic properties of clusters at the nanometer scale is highly challenging because it requires well-characterized systems (in term of structure, surrounding environment…) and involves several techniques. We have found a surprising difference between nanoparticles and the bulk material: the magnetic anisotropy increase accompanying the A1 to L10 transition is much lower for nanoparticles than for the bulk. Using our low energy cluster beam deposition source, we synthesize well-defined CoPt clusters with a diameter around 3 nm. These clusters, pre-formed in gas phase and deposited in ultrahigh vacuum conditions, represent benchmark systems: the samples are made of diluted clusters embedded, in order to avoid coalescence or interparticle interactions, in an amorphous carbon matrix well suited for direct high resolution transmission electron microscopy observations (HRTEM). The transition from the chemically disordered A1 phase to the L10 phase is then obtained by annealing. By combining several techniques, we have been able to reach a quantitative structural determination of the CoPt nanoparticles, together with the magnetic signature of chemical ordering. In particular, while a quantitative investigation of the chemical order parameter has been performed on individual nanoparticles by HRTEM, the evolution of the crystal cell parameters upon annealing has been measured by grazing incidence X-ray diffraction (GIXRD). We observe a A1 to L10 phase transition of all particles, with a tetragonalisation of the cell (c/a ratio of 0.93), and, contrary to the bulk, an increase of the d111 distance. Magnetic measurements on the same samples allow us to study the impact of annealing on the magnetic properties of these nanoparticles. X-ray magnetic circular dichroism measurements (XMCD) reveal a µL/µS increase for both cobalt and platinum atoms, and a strong µS enhancement for cobalt. On the other hand, SQUID magnetometry measurements show that, despite a 100% augmentation, the magnetic anisotropy energy remains much smaller for chemically ordered CoPt nanoparticles than for the bulk L10 phase. Size-selected nanoparticles are now investigated in order to get a better understanding of the size effect both on the structural phase transition and on the magnetic properties. [1] F. Tournus et al. Phys. Rev. B 77, 144411 (2008) [2] The authors acknowledge J.P. Simon, J.F. Bérar, F. Wilhelm, A. Rogalev for they technical help during the synchrotron measurements. [3] Thanks are due to the CLYM (Centre Lyonnais de Microscope) for the access to the transmission electron microscope.

SESSION HH5: Poster Session
Wednesday Evening, April 15, 2009
8:00 PM
Salon Level (Marriott)

HH5.1
Abstract Withdrawn

HH5.2
Manipulating the Morphology of Polymer-Fullerene Bulk Heterojunctions through Selective Solvent Annealing. <u>Eric</u>

Verploegen[1,2], Michael Toney[2] and Zhenan Bao[1]; [1]Chemical Engineering, Stanford University, Stanford, California; [2]Stanford Synchrotron Radiation Laboratory, Stanford Linear Accelerator Center, Menlo Park, California.

Manipulating the Morphology of Polymer-Fullerene Bulk Heterojunctions through Selective Solvent Annealing. The optimization of bulk heterojunction blend morphologies is critical in order to achieve increased performance in organic photovoltaic devices. The nanophase segregated heterojunction domain size must be about the same as the exciton diffusion length in order for efficient conversion of adsorbed photons into electrical current. In addition, the morphology and molecular packing of both the acceptor and donor within their respective domains should be optimized for maximum electron and hole mobilities. Thermal and solvent annealing have shown utility for improving such morphologies. Typically, extended annealing leads to unfavorable coarsening of the acceptor and donor domains, resulting in phase segregation larger than the exciton diffusion length. It is desirable to optimize the morphology/packing - e.g. increase the crystallinity - of these domains without allowing for the size of the domains to grow. We present a selective solvent annealing strategy that allows for each domain to be essentially annealed individually: each domain "locks in" both the nanoscale domain size and optimal morphology/packing. The system is first thermally annealed in order to obtain the desired domain size. By then exposing the blend to solvent vapor that selectively swells the fullerene domains, sufficient mobility is provided to allow for increased crystallization, while the polymer domains prevent the fullerene crystallization from increasing the domain size. A second annealing step, this time with a solvent vapor that is selective for the donor polymer, facilitates crystallization of the polymer domains, while the crystalline fullerene domains prevent coarsening of the domains. The annealing process is monitored in-situ to observe the morphological and structural evolution with grazing incidence diffraction (GID) and small angle X-ray scattering (SAXS) to allow to for effective optimization of the morphologies.

HH5.3
Abstract Withdrawn

HH5.4
Nanostructured Composite of the Binary System W-C on Thin Films Obtained by RF Magnetron Sputtering. Nelcari T Ramirez[1], Angel M Ardila[1] and Victor J Garcia[2]; [1]Grupo de Física Aplicada, Universidad Nacional de Colombia, Bogotá, Cundinamarca, Colombia; [2]Grupo de Física de la Materia Condensada, Universidad de Los Andes, Mérida, Mérida, Venezuela.

The Raman scattering spectroscopy of thin films of the system W-C that were deposited on austenitic steel substrates by RF magnetron sputtering, suggests the existence of a nanostructured composite in the obtained films. In the Raman spectra can be observed that the peaks G and D corresponding to disordered and ordered graphite predominate, indicating the presence of graphitic dominions. Studies of Energy dispersive X-Ray Spectroscopy (EDX) and X-Ray Diffraction confirmed the existence of the phases WC (δ) and W_2C (β) of tungsten carbide in the different films, as well as the existence of the composite, where both graphitic phases and dominions can be found. Measures of adhesion, hardness and grain size were carried out by the scratch test, microindentación Vickers and atomic force microscopy (AFM) techniques, respectively. The mechanical and tribological properties of the films were related as a function of the deposition temperature, chemical composition and grain size. Calculations of the practical work of adhesion indicate that when increasing the substrate temperature, the film-substrate adhesion increases; which can be explained by the diffusion of constituent atoms of the film in the substrate surface.

HH5.5
Characterization of the Interface of SiTiC/TiAl Composites by TEM with or without Interface Modifications. Takakazu Suzuki, AIST, Tsukuba, Japan.

SiC-fiber-reinforced TiAl composites (SiC/TiAl) have attractive attention due to their potential for replacing titanium and nickel-base alloys in aerospace systems such as advanced turbine engines and hypersonic vehicles where specific strength and stiffness at high temperature are critical. The interface layers of SiC/TiAl are believed to contribute strongly to its mechanical properties. A wide variety of interface modifications, such as C, BN, W, or Mo coating or C/W or BN/W double coatings has been applied to the fiber to produce composites, together with the identification of several new interface modification systems, showing promise for high performance fibers and improved composite properties. A research from a perfect cross-sectional view to get more direct and reliable interfacial information especially about bonding around the fiber circumference, has been limited partly due to the difficulty of preparing suitably thin TEM specimen without damaging the interface layers. We report our preparation method for a perfect cross-sectional TEM specimen of SiC/TiAl and the interface characterization results. Single SiC-based Si60%-Ti2%-C15%-O11% fiber (SiTiC) ~11μm in diameter containing about 2% Ti to improve its thermal stability has been used as a reinforcement. Chemical vapor deposition or sputtering has been used to deposit C or TiAl layer. C layer has been deposited uniformly around the fiber at a thickness of about 100 nm and TiAl coating at about 1400 nm. C layer consisted of large amounts of micro crystals of about 1-30 nm. TiAl layer consisted of crystals of about 60-360nm. The specimen has been annealed at 1173 K for 2 hrs in Ar, and prepared by sandwiching and 3mm disks obtained by ultrasonic drilling and mechanical polishing to ~100 μm. Those disks have been further ground by a dimpler to ~10 μm, and argon-ion-etching for 25-30hrs with GATAN 600 to get an electron-beam-transparent foil. H-9000UHR II TEM accelerrating voltage 300 kV, equipped with EDX (electron prove 1nm) has been used. Interfacial reaction and diffusion mainly occurred in the interface between the C layer and SiTiC fiber and the C and TiAl layers. No direct reaction or diffusion occurred between the SiTiC fiber and TiAl layer. Espesially, small amounts of needle-like compound assigned as Aluminum Titanium Carbide, (Ti3AlC)5C, propagating into the fiber has been found at the interface area without any coating layer. The existance of the compound is indicating there are reaction and diffusion products of SiTiC fiber and TiAl. Such Aluminum Titanium Carbide penetrating into the fiber seems to induce new stress concentration and generate new cracks in the fiber and degrade the fiber and the composite strength. Combined with those tensile testings of SiTiC/TiAl with or without interface modification with Weibull statistic analysys reported previously, we would like to discuss those effectiveness of variuos types of interface modifications with TEM observation.

HH5.6
Quantitative Characterization of Micro- and Nano-scale Deformation of Solids. <u>Vitaly Shpeizman</u> and Nina Peschanskaya; Ioffe Physical-Technical Institute of the Russian Academy of Sciences, Saint-Petersburg, Russia.

The multilevel character of deformation and its localization at different levels is a concept that has been recognized for several decades. However, the process has until now been described only by the average velocity of deformation at the macrolevel. In the traditional techniques of deformation recording, small-scale non-uniformities are averaged out and made invisible. A new method of studying deformations using a laser interferometer makes it possible to observe small deformation jumps and to measure their characteristics. In our experiments, the velocity of the deformation of a sample is found from the interferometric data of a row reflected from the movable edge of the sample and a reference row. The obtained interferogram consists of sequential beats with a period corresponding to a deformation increment of 300 nm. The frequency of the intensity signal is proportional to the current strain rate. Experiments show that interferograms represent the repeated parts with relatively high and low strain rates. The change in the period of strain rate measured in terms of deformation units in many cases correlates with the size of inhomogeneities in the sample structure. To reveal deformation jumps of 150 nm or more, periodic changes in the strain rate were measured at the base of each half of sequential beats in an interferogram, and the dependence of the strain rate on the deformation increment was plotted. Strain rate instability within the beat period was analyzed by comparing the experimentally determined dependence of interferometry intensity on the deformation time with the single frequency dependence (I~cos(wt)), for some part of the period. This technique allows the observation of deformation inhomogeneities of 50-150 nm. We studied nanocrystalline metals (Al, Cu, Ti, Fe), polymers (PMMA, PE and others) and ceramics with nanoparticles. All metals were produced by multiple equal-channel angular pressing (ECAP). Polymers were strengthened by nanoscale particles or irradiation. The region of microplasticity was investigated, the stresses being considerably less than the yield point or fracture point. The role of large deformations was studied on samples which were first deformed up to high strains. It was estimated that the nonuniformity of deformation (its small periodic jumps) is the characteristic feature of deformation at all scales: from nano- to macroscale. First, the nanoscale jumps of deformation were detected. Two characteristics of nanojumps - the jump height and the relation between strain rates at slow and rapid phases of the jump - were measured for different materials. The jump height correlates with the size of structural units which take part in the process of deformation at all structure levels. We believe the result obtained may be useful not only for characterization of bulk nanostructural materials but nanodimensional (films, interfaces and others) subjects as well.

HH5.7
Quantitative Characterization of Nanomaterial Dispersion. <u>Shiren Wang</u>[1] and Jingjing Qiu[2]; [1]Industrial Engineering, Texas Tech Univ, Lubbock, Texas; [2]Chemical Engineering, Texas Tech Univ, Lubbock, Texas.

Nanoscale materials, such as fullerene, carbon Nanotubes, graphene, and other metallic nanoparticles, tend to form big clusters due to their large specific surface. It is a big challenge to disperse them uniformly in the matrix and it is also very difficult to characterize the morphology quantitatively. Up to now, there is no attempt found to quantitatively characterize the dispersion results. In this paper, we propose an innovative method to quantitatively characterize the nanoparticle dispersion in the polymer matrix. High-resolution scanning electron microscopy (SEM) or atomic force microscopy (AFM) characterization of nanostructured material samples result in images consisting of distributed nanoscale crystals. In each image, uniformly distributed reference points were generated by the Poisson-process to match the number of nanoparticles observed in the SEM or AFM image in order to guarantee accuracy. The distance between reference points to nanoparticles was calculated and each nearest neighbor distance was normalized to eliminate the effect of density of nanoparticles in the cross-section area. A dispersion index was defined as a deviation of normalized observed nearest neighbor distance. A smaller index means smaller deviation from ideal uniformity and represents more uniform dispersion. Each sample was characterized by SEM and resulted in many images. Average dispersion index from all the images derived from the same sample was used to quantify their dispersion in the specific sample. With the quantified dispersion, the effect of surface-functionalization on carbon nanotubes dispersion was investigated, and it was found the dispersion index is dependent on the surface modification method and functionalization degree. The correlation of functionalization degree with dispersion index was quantified. In addition, a quantitative structure-property relationship in carbon nanotube composites was achieved, providing insight to the nanostructured materials design, fabrication and applications.

HH5.8
Size Dependence of Nanoparticle Dissolution in a Matrix: Gold Particles in Bismuth. <u>Parasuraman Swaminathan</u>, Shankar Sivaramakrishnan, Jacob S Palmer and John H Weaver; Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois.

We discuss the dissolution and phase transformation of Au nanoparticles buried in a Bi matrix as a function of their size. This information allows us to understand the stability of nanoparticles embedded in a matrix. The particles were formed by vapor deposition onto Bi films at room temperature. Subsequently, they burrowed into Bi because of its lower free energy compared to Au and the minimal interfacial energy in this system. At room temperature, burrowing is competitive to particle growth. Since burrowing constantly removes particles from the surface, arriving adatoms diffuse longer and attach to the remaining particles, broadening the size distribution. Post deposition, particles on the surface complete their burrowing. The bulk phase diagram of Au-Bi indicates negligible solid solubility, with an intermetallic, Au2Bi, forming above 120 °C. We have investigated the formation of Au2Bi during annealing by using in-situ transmission electron microscopy and nano beam electron diffraction. Initially, the Au particles dissolve into the Bi matrix to give a solid solution. This is followed by the formation of Au2Bi. We have studied the dissolution kinetics by measuring its rate as a function of particle size at different temperatures and have used these results to

calculate the activation energy for this process, which is the energy required for an atom to detach from the particle.

HH5.9
Raman Topography and Strain Uniformity of Large-Area Epitaxial Graphene. Joshua A Robinson[1,2], Conor Puls[3], Neal Staley[3], Joseph Stitt[2], Mark Fanton[1], Konstantin Emtsev[4], Thomas Seyller[4] and Ying Liu[3,2]; [1]Materials Division, Penn State Electro-Optics Center, University Park, Pennsylvania; [2]Materials Research Institute, Penn State University, University Park, Pennsylvania; [3]Physics, Penn State University, University Park, Pennsylvania; [4]Lehrstuhl für Technische Physik, Universität Erlangen-Nürnberg, Erlangen, Germany.

Graphene exhibits extraordinary electronic properties including an unusually high mobility of the charge carriers. Significant progress toward understanding the properties of graphene has resulted from studying graphene flakes mechanically exfoliated from bulk graphite. While these small flakes (< 100 um^2) are suited for studying the fundamental science of graphene, they are not practical for the development of graphene-based technologies. Alternatively, the sublimation of silicon (Si) from silicon carbide (SiC) to form epitaxial graphene is a promising route for the production of wafer size graphene films. Rapid characterization and precise control of properties of epitaxial graphene over a wafer-size area, which are yet to be achieved, are necessary for developing a graphene based technology. Micro-Raman spectroscopy, a rapid, optical characterization technique, was used first on few-layer graphene flakes prepared by mechanical exfoliation, followed by a spatially resolved study. Raman spectroscopy measurements have also been used on epitaxial graphene, yielding important information on the thickness, the charge carrier density, and the strain. However, no studies of Raman topography, the two-dimensional mapping of Raman spectrum over large-area epitaxial graphene, have been carried out to date. We report results of Raman spectroscopy studies of large-area epitaxial graphene grown on SiC. Our work reveals unexpectedly large variation in Raman shift resulting from graphene strain inhomogeneity, which is shown to be correlated with physical topography by coupling Raman spectroscopy with atomic force microscopy. We show that graphene strain can vary over a distance shorter than 300nm, and may be uniform only over roughly 1 um. We show that nearly strain-free graphene is possible even in epitaxial graphene.

HH5.10
Abstract Withdrawn

HH5.11
Spectroscopic Raman Nanometrology of Suspended and Supported Graphene Ribbons Irene Gonzales Calizo, Muhammad Rahman and Alexander A Balandin; Electrical Engineering and Materials Science and Engineering Program, University of California - Riverside, Riverside, California.

Micro-Raman spectroscopy is an effective tool for graphene characterization. However, most of the Raman spectroscopy studies of graphene were limited to graphene layers on silicon/silicon-oxide substrates with a carefully selected thickness of the oxide layer. For quantitative characterization of graphene nanostructures and for graphene device applications it is important to investigate how the Raman signatures from graphene are affected by different substrates. Another important issue is the influence of the width of a graphene ribbon and the edge states on the Raman spectrum. Here we review our recent results of the investigation of a large number of graphene flakes and ribbons on various substrates or suspended across trenches in silicon wafers. The number of atomic layers in the examined samples was confirmed by the atomic force microscopy and analysis of the 2D-band in Raman spectrum [1]. We investigated Raman spectra from graphene layers on GaAs, sapphire and amorphous glass substrates and compared them with those from graphene on the standard silicon substrate and graphene flakes suspended over trenches in the wafers. The weak influence of the substrates on the Raman spectra was explained by the polarization and dispersion features of the main phonon branches in graphene. We also studied the effect of temperature on the most characteristic peaks in the Raman scattering spectra of graphene. The measurements were carried out with the external control of the sample temperature. We observed the red shift of G peak of graphene with increasing temperature despite anomalous temperature expansion of the graphene crystal lattice. The value of the temperature coefficients for the G-band peak of the single-layer graphene is -1.6×10-2cm-1/K [2]. The obtained temperature coefficients of graphene Raman peaks allowed us to carry out the first measurements of the thermal conductivity of graphene [3]. A comparison of Raman spectra for the suspended graphene ribbons with those of the supported ribbons and flakes allowed us to further expand the use of Raman spectroscopy as quantitative characterization, i.e. nanometrology, tool for graphene nanostructures. The work in Balandin group was supported, in part, by DARPA - SRC Focus Center Research Program (FCRP) through its Functional Engineered Nano Architectonics (FENA) center and Interconnect Focus Center (IFC). The initial experimental work was done in cooperation with Prof. C.N. Lau (UCR). [1] I. Calizo, W. Bao, F. Miao, C.N. Lau and A.A. Balandin "The effect of substrates on the Raman spectrum of graphene: Graphene-on-sapphire and graphene-on-glass," Appl. Phys. Lett., 91, 201904 (2007). [2] I. Calizo, A.A. Balandin, W. Bao, F. Miao and C.N. Lau, "Temperature dependence of the Raman spectra of graphene and graphene multi-layers," Nano Letters, 7, 2645 (2007). [3] A.A. Balandin, et al., "Superior thermal conductivity of single-layer graphene," Nano Letters, 8, 902 (2008).

HH5.12
A Comprehensive Approach for Quantitative Characterization of Nanosturctures by Scanning Probe Microscopy Amjed Al-mousa[1,2], Darrell L Niemann[1], Norman G Gunther[1] and Mahmud Rahman[1]; [1]Electron Devices Laboratory, Electrical Engineering, Santa Clara University, Santa Clara, California; [2]PDF Solutions, San Jose, California.

Nanoporous and nanocrystalline materials are becoming increasingly important in emerging devices and systems. In order to fully understand the functional properties of the nanostructures in such systems, it is necessary to quantify structural information

associated with external surfaces at multiple length scale employing a combined approach. In this paper, an analysis methodology based on our recently developed feature recognition algorithm is presented. This algorithm isolates surface nanostructures and extracts quantitative information such as their shape and size. The algorithm is independent of feature size, and does not require any data-dependent threshold. Here, we successfully employed the algorithm to analyze Atomic Force Microscopy (AFM) data and extracted information about features on the order of tens of nanometers. The algorithm, however, can easily be adapted to process other types of Scanning Probe Microscopy (SPM) measurements. In order to identify the salient features of the surface, a moving average filter is deployed once vertically and then horizontally. The height and slope data along the scan lines and perpendicular to it are then processed separately to identify features such as hills, valleys, and flat areas in each direction. This process identifies regions that correspond to surface structures of interest, which we call Potential Structure Points (PSP). Next, the horizontal and vertical data are overlaid and points which are recognized both horizontally and vertically as PSPs are classified as Structure Points (SP). A clustering algorithm then sweeps the data to organize neighboring SPs into structures. Any discontinuities that may appear in the AFM data due to hysteresis are corrected by the algorithm by calculating the shift in the average of each scan line, and then statistically identifying the lines that show anomalous shifts. Once identified, these scan lines are biased to eliminate the discontinuities. Further, since the measured AFM data are strongly influenced by the size and shape of the AFM tip, our algorithm considers the convoluting effect of the tip shape on sharp edges. In summary, we have developed and tested an algorithm for analyzing surface nanostructures which is independent of the shape and size of surface features. It is robust to entire classes of data anomalies, such as the raster discontinuities which frequently occur due to substrate hysteresis or to instrument vibration. Probe tip size and shape effects have important impact on the minimum curvature radii which can legitimately be expected in processed data. These expectations have been borne out quantitatively in our tests with AFM data. We apply our methodology to analyze AFM data for crystalline films of organic semiconductors.

<u>HH5.13</u>

X-ray Scattering Study of Interface Evolution and Grain Growth in Encapsulated Cu films Andrew P Warren[1], Yao Bo[1], Tik Sun[1], Katayun Barmak[2], Michael F Toney[3] and <u>Kevin R Coffey</u>[1]; [1]Advanced Materials Processing and Analysis Center, University of Central Florida, Orlando, Florida; [2]Department of Materials Science and Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania; [3]Stanford Synchrotron Radiation Laboratory, Menlo Park, California.

The scattering of electrons by surface roughness and grain boundaries have been considered as key contributors to high resistivity in Cu interconnects as the conductor dimensions approach the mean free path of the conduction electrons. To study the influence of annealing on interface roughness, a series of Cu thin films with thicknesses of 28 to 158 nm, encapsulated in SiO_2 and Ta/SiO_2, were sputter deposited onto thermally oxidized Si wafers. The samples were annealed at 150°C and at 600°C following deposition. Specular x-ray reflectivity was used to separately determine the root mean square roughness for both the upper and lower Cu interfaces. The lateral correlation length of the roughness was studied by diffuse x-ray reflectivity and grazing incidence small angle x-ray scattering. The roughness of the lower SiO_2/Cu interface was constant at an average 1.0±0.1 nm, independent of annealing temperature. By contrast, the roughness of the upper Cu/SiO_2 interface decreased from 1.0±0.1 nm to 0.35±0.05 nm upon annealing at 600°C. Such a reduction in roughness with annealing was not observed in the $SiO_2/Ta/Cu/Ta/SiO_2$ samples. The lateral correlation length scaled with thickness for all samples, and annealing at 600°C resulted in a longer lateral correlation length. Grazing incidence X-ray diffraction was used to determine the in-plane grain size of the Cu films. This is quantitatively compared to separate grain size measurements performed on the same set of samples using transmission electron microscopy (TEM), wherein hollow cone dark field imaging was utilized to provide enhanced diffraction contrast. Agreement between the TEM and X-ray measures of average grain size is observed for samples with grain size below 80nm.

<u>HH5.14</u>

Polymeric Hydrophobic Gold Nanoparticles for Optical and X-ray Computed Tomography Imaging Contrast Agent.
<u>Yoonah Kang</u>[1], Eun-Kyung Lim[1], Jin-Suck Suh[2], Yong-Min Huh[2] and Seungjoo Haam[1]; [1]Department of Chemical Engineering, Yonsei University, Seoul, Korea, South; [2]Department of Radiology, Yonsei University, Seoul, Korea, South.

Gold nanoparticles (GNPs) can absorb and scatter the electromagnetic radiation induced from x-ray and enhance their intensities because of strong electric fields at surface. A new computed tomography imaging agent, GNPs not only overcome these limitation but has a higher atomic number and a higher absorption coefficient than iodine (common CT contrast agent). Furthermore, polymer coated GNPs permit longer imaging times since they have longer circulation time. In this study, we synthesized polymeric hydrophobic gold nanoparticles (PHGNs) to serve as nano-probes for optical and x-ray computed tomography imaging contrast agent for breast cancer detection. First, hydrophobic GNPs were synthesized by reduction of tetrachlroloaurate(III) trihydrate, in the presence of sodium borohydride, tetraoctylammonium bromide, and dodecanethiol (DdSH). The refined product was dissolved in chloroform using coated with DdSH because the terminal thiol group of dodecanethiol has a strong attachment to GNPs. Water dispersion polymeric hydrophobic gold nanoparticles were then finally obtained by the encapsulation of hydrophobic GNPs with sodium dodecyl sulfate (SDS) as an amphiphilic surfactant by nanoemulsion method. The morphology of PHGNs was evaluated by transmission electron microscopes and scanning electron microscopic and revealed that DdSH-GNPs were successfully encapsulated by SDS. The DdSH-GNPs was soluble only in chloroform and the PHGNs were dispersed only in distilled water due to the hydrophilic portion of SDS or phase transfer phenomena. PHGNs were demonstrated excellent colloidal stability in water phase because of repulsion force of SDS coated DdSH-GNPs (PHGNs). The chemical structure of the synthesized PHGNs was confirmed by FT-IR. These results suggested that the DdSH-GNPs existed successfully in PHGNs. The quantity of GNPs in PHGNs was measured using a thermogravimetric analyzer. The quantity of GNPs encapsulated in PHGNs was 49.2wt% (25% dodecanethiol, 25.8% SDS). The crystallinity of GNPs in the PHGNs could be evaluated using X-ray diffraction patterns. The surface charge and size distribution of prepared PHGNs were analyzed using dynamic light scattering.

The size distribution and zeta potential value of PHGNs were 133 ± 1.1 nm and -13.5 ± 1.4 mV, respectively. We performed a MTT assay to examine the cellular cytotoxicity of PHGNs. A MTT assay was performed using NIH3T3 and NIH3T6.7 cells treated with PHGNs. Furthermore, the scattering image for well-distributed GNPs in the PHGNs can be obtained by dark-field microscopy. We calibrated the x-ray absorption of the PHGNs to investigate CT contrast efficacy of PHGNs. The maximum HU value of PHGNs was reached at 954.9 HU. This result clearly indicates that the PHGNs have a high potential for use in vivo CT imaging. Consequently, these results demonstrate that synthesized PHGNs have highly versatile biomedical characteristic such as optical and x-ray computed tomography imaging contrast agent.

HH5.15
Characterization of Boron Nitride Films Growth by Chemical Vapor Deposition. <u>Jose Eneider Nocua</u>[1,2] and Gerardo Morell[1,2]; [1]Physics, University of Puerto Rico, Rio Piedras, Puerto Rico; [2]Institute for Functional Nanomaterials, San Juan,, Puerto Rico.

Boron nitride nanotubes (BNNT's) shown an insulating character, independent of their diameter and helicity. Are structural analogues of carbon nanostructures, chemically inert, and potentially important in mechanical applications that include the strengthening of light structural materials for the aerospace industry. Using borazine (B3N3H6) as a precursor and technique of chemical vapor deposition and maintaining the temperature of the heater at 800oC for 30 minutes were deposited on silicon substrates boron nitride films. Their morphology was examined by scanning electron microscope (SEM) and transmission electron microscopy (TEM), while its chemical composition was studied by techniques scanning electron microscopy energy dispersive (EDS), Fourier transform infrared spectrometry (FTIR), electron energy loss spectroscopy (EELS) and, X-ray photoelectron spectroscopy (XPS). These results indicate that the material that is obtained is BN with hexagonal structure.

HH5.16
Synthesis Processing And Characterization Of CU-CNT Nano-Composites Martin Emilio Mendoza, <u>Guillermo Solorzano</u> and Eduardo Brocchi; Metallurgic and Materials, PUC-Rio, Rio de janeiro, Rio de Janeiro, Brazil.

The increasing interest in nanostructured materials in recent years has provided incentive to develop new synthesis procedures aiming at obtaining important amounts of this type of material. Leading this effort a new category of materials: carbon nanotubes (CNT)- containing metal-matrix nanocomposites1,2,3. Such motivation relies on the well-established superior mechanical and transport properties of CNT4, In the former CNT exhibits a Young's modulus of 1 TPa and a tensile strength of 30Gpa 5 , thereby as an ideal reinforcing additive in composites. In the present work, copper matrix nano composite with carbon nanotubos (2% wt) was produced by chemical synthesis method 6,7. The procedure begins by the copper nitrate dissociation containing SWCNT and anionic tensoactive agent at 250°C, followed by in-situ reduction at 350°C, under hydrogen atmosphere at pressure of 1atm. CuO and Cu formation was confirmed by X ray diffraction at the moment of dissociation and reduction respectively. CNTs presence was detected at both steps by this characterization method. Transmission Electron Microscopy analysis, estimate particles grain size of 30nm for CuO powder while Cu powder particles were observed to be in the 100-300nm range, showing good dispersion of CNT. Bulk nano-composite pellets of the reduced material were obtained by pre-compactation under uniaxial pressure of 17 MPa followed by issostatic pressure of 150MPa. Sinterizing of the compacted material was carry out at 650°C under Argon atmosphere by 15 min. Scanning Electron Microscopy and Transmission Electron Microscopy analysis of the sinterized material showed an heterogeneous grain size distribution in the 100nm to 4 um range. Electric resistivity measures show that the nanocomposite material has lower resistivity at low temperature (2x10-6 ohm.cm) at 83°K than the copper without carbon nanotubes (5.9x10-6 ohm.cm). Vickers micro hardness measures, indicate a considerable increasing of hardness of the composite material with CNTs (70HV) when it is compared with copper without nanotubos(32HV), processed at the same conditions. 1 Cornelia Otto. Synthesis and Characterization of CNT Reinforced Copper Thin Films. Dissertation Stuttgart University. Bericht Nr. 194 November 2006. 2 J.P. Tu, Y.Z. Yang, L.Y. Wang and X.B. Zhang Tribology letters Vol 10 No4, 2001. 3 William A. Curtin and Brian W. Sheldon.. Materialstoday November 2004. 4 K. T. Kim et al., Materials Science and Engineering A 449-451 (2007) 46-50 5 P. Quang, S.C. Yoon, Materials Processing Technology187-188 (2007) 318-320. 6 P. Ayala, F.L. Freire, , David J. Smith, I.G. Solorzano. Chemical Physics Letters 431(2006) 104-109. 7 P.K. Jena, E.A. Brocchi, M.S. Motta. Materials Science & Engineering A313(2001) 180-186.

HH5.17
In-situ Synchrotron X-ray Scattering Study on the Initial Structure of Ruthenium Atomic Layer Deposition Films for the Electronic Devices. <u>Yong Jun Park</u>[1,2], Han-Bo-Ram Lee[2], Woo-Hee Kim[2], Dong-Ryeol Lee[4], Hyungjun Kim[2], Shi-Woo Rhee[3] and Sunggi Baik[2]; [1]Beamline division, Pohang Accelerator Laboratory, Pohang, Gyeongbuk, Korea, South; [2]MSE, POSTECH, Pohang, Gyeongbuk, Korea, South; [3]CE, POSTECH, Pohang, Gyeongbuk, Korea, South; [4]Physics, Soongsil Univ., Seoul, Korea, South.

We report microstructures of initial growth of ruthenium (Ru) films, which were prepared by Atomic Layer Deposition (ALD) method. Ru is a promising material as an adhesion layer or diffusion barrier of copper interconnect in semiconductor electronic device. As devices scale down, the ALD is expected to play an important role for the next generation MOSFET due to its excellent step coverage and precise thickness control. To characterize the microstructure and physical properties during ALD growth, we used the in-situ ALD growth chamber, installed on the diffractometer at 3C2 XRD beamline in Pohang Light Source. Since the ALD growth is strongly dependent on the initial surface state and reaction, we concentrate on the initial structures. Synchrotron X-ray scattering measurement with high photon flux allowed us to characterize the microstructure of 1~2 nm films at initial growth stage, nondestructively. Significant differences between in-situ and ex-situ X-ray scattering measurement will be displayed. And also, we show the strong point of X-ray scattering measurement compare with the conventional methods. The results obtained by

the X-ray scattering measurement are consistent with the SEM results. X-ray scattering analysis can be applied an inline characterization method for industry to measure physical morphologies.

HH5.18

Theoretical Study of Adsorption and Thermal Desorption of Fullerenes on the Crystal Surface. Svetlana Yurievna Zaginaichenko and Zinaida A Matysina; 67, Institute for Problems of Materials Science of NAS of Ukraine, Kiev, Ukraine.

A statistical theory of adsorption and thermal desorption of fullerenes in a multi-layer fullerite film on a crystal surface has been developed. These processes for multi-layer film of fullerenes of different kinds (hollow C_{60}, C_{70} or endohedral $M@C_{60}$, $M@C_{70}$ or hydrogenated $C_{60}H_n$, $C_{70}H_n$, n > 36) evaporated on the free plane of crystal have been investigated. The calculation of the free energy of the system has been carried out by the method of average energies in approximation of pair interaction between nearest fullerenes and fullerenes with atoms of crystal substrate and also in assumption of geometrical ideality of structures both of substrate and fullerite film. The equilibrium fullerene concentration has been calculated as a function of temperature, film thickness and energy constants of the system. The temperature of desorption its dependence on film thickness have been evaluated. The limitary concentration of fullerenes for different numbers of monolayers has been found. The considerable increase of concentration of adsorbed fullerenes with a rise of film thickness at low temperatures has been justified. The developing processes of adsorption with increase in temperature and desorption at a high temperatures, which were observed experimentally, have been validated.

HH5.19

The Structure of Amorphous Calcium Phosphate - a Key Intermediate in Skeletal Calcification. Kate Wetherall[1], Richard Haworth[1], Richard Martin[1], Robert Moss[1], Danielle Laurencin[2] and Gavin Mountjoy[1]; [1]School of Physical Sciences, University of Kent, Canterbury, Kent, United Kingdom; [2]Department of Physics, University of Warwick, Coventry, United Kingdom.

Research into the process of bone calcification has studied the transformation of calcium and phosphate ions into hydroxyapatite and has identified an intermediate amorphous phase. The precipitate known as Amorphous Calcium Phosphate (ACP) has the approximate composition $Ca_3(PO_4)_2.nH_2O$ but its local structure is unknown. The only structural studies carried out were performed decades ago with lab based equipment. They theorised the material was composed of clusters in the order of 10Å, but this hypothesis has never been proven. Presented here are the initial results of a complete structural study of ACP using diffraction, absorption spectroscopy, small angle scattering, microscopy and many more techniques. Results so far have already revealed structure on several length scales. It is hoped that if the structure of this material can be fully understood then it will improve the understanding of the reaction between biomaterials and the body and hence aide in their development.

HH5.20

Low Energy Electron Microscopy of Ge Deposition on Unpatterned and Patterned Si (001) Surfaces. Jacob C Thorp[1], Jeremy F Graham[1], Jerrold Floro[1] and Robert Hull[2,1]; [1]Materials Science & Engineering, University of Virginia, Charlottesville, Virginia; [2]Materials Science & Engineering, Rensselaer Polytechnic Institute, Troy, New York.

Low Energy Electron Microscopy (LEEM) using a SPECS P90 system has been used to observe the growth of Ge wetting layers and quantum dots on patterned and unpatterned Si (001). LEEM allows for in situ growth of thin films (in this case, deposition of Ge from an effusion cell) to be observed in real time with image acquisition rates as low as tens of ms and lateral spatial resolutions of ~ 5-10 nm. Diffraction contrast imaging using the orthogonal 2x1 and 1x2 reflections from the reconstructions of the Si (001) surface in the Low Energy Electron Diffraction (LEED) pattern enables high contrast imaging of surface domains and intervening atomic steps.[1] Our LEEM experiments on unpatterned surfaces enable us to study the atomic evolution of the surface structure during Ge wetting layer deposition. In particular we are studying the relative degrees of terrace nucleation vs. step attachment during Ge wetting layer growth, and examining the evolution of surface step roughness following previous STM studies that show reversal of type SA and SB step roughness during wetting layer growth.[2] We are also studying the evolution of the Ge wetting layer and subsequent quantum dot nucleation on surfaces that are patterned with a focused ion beam (FIB). In particular, we pattern the Si surface with a mass selecting FIB that enables generation of a silicon ion beam from an AuSi source to ensure that the surface is not locally doped as it would be for a conventional Ga ion beam. In this manner we also eliminate any role of chemical effects on the templating associated with the localized FIB surface treatment. Following in-situ cleaning of the patterned Si(001) surfaces, LEEM shows highly ordered terraces with large, preferentially directed surface domains around the ion patterned areas. These large area domains are expected to have significant effects on the nucleation of Ge quantum dots on the FIB template sites, as adatoms landing on terraces then typically have to cross very few (if any) steps to reach quantum dot nucleation sites at the FIB pits. This may have significant ramifications for our previous studies of templated Ge quantum dot growth on FIB patterns,[3] and should enable us to develop additional insight into the correlation of quantum dot nucleation kinetics (e.g. the effects of capture zone size) to the detailed local surface structure. 1. R.M. Tromp, IBM J. Res. Dev. 44, 4 (2000) 2. Feng Liu, Fang Wu, M.G. Lagally, Chem. Rev., 97, 1045 (1997) 3. A Portavoce et al, Nanotechnology 17, 4451 (2006)

HH5.21

High Resolution TEM Lattice Imaging of Lead Chalcogenide|Cadmium Chalcogenide Colloidal Nanoparticles Karel Lambert, Bram De Geyter, Iwan Moreels and Zeger Hens; Physics and Chemistry of Nanostructures, Ghent University, Gent, Belgium.

Covering colloidal semiconductor quantum dots (QDs) with an inorganic shell of a second material has become a popular

approach to tailor the optical properties of these nanomaterials. If the energy levels of the shell encompass those of the core (type 1 band alignment), this results in nanoparticles with an enhanced and stable luminescence quantum yield. A staggered band alignment (type 2) offers much more possibilities since it leads to a spatially separated exciton which feature, for instance, a much lower threshold for light amplification [1]. Core|shell particles are typically made by growing additional material on top of the initial core particle. An apparently straightforward alternative is offered by cationic exchange, where a core|shell particle is grown by partial replacement of the initial cations in the core by others [2]. In this contribution, we use high resolution TEM lattice imaging of PbTe|CdTe and PbSe|CdSe core|shell QDs to evaluate this procedure. First, we show that the slight difference in lattice constant enables the simultaneous imaging of the core and the shell crystal lattice. These images demonstrate that the zincblende CdTe and CdSe shells are fully aligned with the rocksalt PbTe and PbSe cores, suggesting that either the anionic or the cationic sublattice continues coherently throughout the whole heterostructure. Second, we find that core and shell are preferentially separated by {111} interfaces. Since the {100}, {110} and {111} interfaces have similar interfacial energy [3], this points towards an anisotropic growth mechanism. This anisotropy is reflected in a strong increase in sample heterogeneity. We find that cationic exchange leads to a variety of core sizes, core shapes and core positions, from central, quasi-spherical cores to completely eccentric, elongated structures. We conclude that cationic exchange is not as straightforward an approach to make colloidal core|shell QDs particles as it may seem, and that high resolution structural characterization is crucial to its evaluation. [1] Klimov, V. I., Ivanov, S. A., Nanda, J., Achermann, M., Bezel, I., McGuire, J. A., Piryatinski, A., Nature 447, 441-446 (2007). [2] Pietryga, J.M.; Werder, D.J.; Williams, D.J.; Casson, J.L.; Schaller, R.D.; Klimov, V.I.; Hollingsworth, J.A. J. Am. Chem. Soc. 2008 130, 4879-4885 [3] Leitsmann, R.; Ramos, L.E.; Bechstedt, F. Phys. Rev. B 2006 74, 085309

HH5.22
Abstract Withdrawn

HH5.23
Strained Silicon Nanomembranes using a Polycrystalline Silicon Nitride Stressor. Anna Clausen, Donald E Savage, Chanan Euaruksakul, Chen-Chun Chen and Max G Lagally; Materials Science, University of Wisconsin, Madison, Wisconsin.

Strained (001) silicon nanomembranes have recently been produced through epitaxial growth of SiGe stressor layers, with strain up to 1% in the Si layer [1]. These nanomembranes provide flexible, transferable Si with increased electron mobility. Currently, this technique relies on expitaxial growth of the stressor layer by chemical vapor deposition (CVD) or molecular beam epitaxy, techniques that are sensitive to surface conditions and that require great care during growth. We strain thin Si layers in silicon-on-insulator (SOI) using instead a polycrystalline silicon nitride (SiN) stressor layer, grown by plasma-enhanced CVD (PECVD), covering the whole surface. The strained Si can then be released from the buried oxide and transferred to a new substrate. PECVD growth proves to be less sensitive to surface conditions and has several free parameters to control the stress of the nitride layer, from tensile to compressive. Previous efforts to incorporate strain in the template layer of SOI with polycrystalline SiN have been made with low-pressure CVD for terrace [2] and ledge and beam shapes [3]. Our technique is unique because the full release of SiN/Si layers from the oxide creates elastically strain-shared Si nanomembranes that can then be transferred and bonded flat to a new substrate. We analyze the strain in transferred nanomembranes with high-resolution x-ray diffraction (XRD) and Raman spectroscopy. The presence of thickness fringes in XRD indicates the membranes relax elastically without appreciable dislocation formation. Raman spectroscopy confirms the uniformity of strain and its magnitude. Transmission electron microscopy and low-energy electron microscopy are used to examine the Si films for dislocations at densities below what XRD can see. Results are in good agreement with predictions of continuum elasticity theory. This work is supported by the DOE. [1] Roberts, M. et al., Nature Mat. 5, 388-393 (2006). [2] Kosemura, D. et al., J. Electrochem. Soc. 6, 245-250 (2007). [3] Tanaka, M. et al., App. Surf. Sci. 254, 6226-6228 (2008).

HH5.24
Initial Growth Structure of Ge on GaAs(001). Jun Nara[1], Akihiro Ohtake[2] and Takahisa Ohno[1]; [1]CMSC, National Institute for Materials Science, Tsukuba, Japan; [2]QDC, National Institute for Materials Science, Tsukuba, Japan.

The heterovalent interface between a group IV elemental semiconductor and a III-V compound semiconductor may cause the charge depletion or the charge oversaturation by 0.25 electron, according to simple bond charge picture. For the polar (001) and (111) orientations of the ideally abrupt interfaces, such electrically charged defects give rise to the formation of a macroscopic electric field, which make the interface unstable. In order to achieve the charge neutrality at the interface, redistributions of the charge and/or atomic rearrangements are required. However, little is known as to how the heterovalent interfaces are formed. It is known that at the initial stage of the Ge growth on GaAs(001), a reconstructed structure with a (1x2) periodicity is formed [1-3]. A structure model built up with Ga-Ge dimer on the As-terminated (001) surface has been proposed for the Ge-induced (1x2) reconstruction [2], and has been found to be stable by first-principles calculations [4]. On the other hand, the previous studies have shown that the As atoms segregate to the growing Ge surface [1,3], suggesting that the formation processes of the interface is more complicated. We have reexamined the atomic structure of the Ge-induced (1x2) reconstruction experimentally and theoretically. We show that the initial growth of Ge on GaAs(001) drives the deposited Ge atoms to subsurface sites and segregates the underlying As atoms at the outermost layer, forming the GaAs(001)-(1x2)-Ge reconstruction consisting of Ga-As dimers. We confirmed that this atomic geometry is energetically favored compared with the previously proposed Ga-Ge dimer model, by using first-principles calculations. Our proposed structure model accounts well for the experimental results from scanning tunneling microscopy (STM), x-ray photoelectron spectroscopy (XPS), and reflection high-energy electron diffraction (RHEED). [1] B. J. Mrstik, Surf. Sci. 124, 253 (1983). [2] X.-S. Wang, K. Self, V. Bressler-Hill, R. Maboudian, and W. H. Weinberg, Phys. Rev. B 49, 4775 (1994). [3] J. R. Power, P. Weightman, and A. A. Cafolla, Surf. Sci. 402-404, 566 (1998). [4] G. P. Srivastava and S. J. Jenkins, Surf. Sci. 352-354, 416 (1996).

HH5.25
Hollow Nickel Oxide Nanoparticles Synthesized by Polystyrene-Assisted Solution Method. <u>Mohammad Vaseem</u>, Dong Min Hong, Jin Hwan Kim and Yoon-Bong Hahn; School of Semiconductor and Chemical Engineering, Chonbuk National University, Jeonju, Korea, South.

Hollow nickel oxide nanoparticles have been synthesized via simple solution method by using polystyrene as a sacrificial template. Firstly, nickel material coated over polystyrene spheres, and further calcinations of nickel-coated polystyrene spheres at 450 0 C resulted hollow nickel oxide nanoparticles. The crystallinity and structural properties of as synthesized nickel oxide nanoparticles were characterized by X-ray powder diffraction (XRD), transmission electron microscope (TEM), high-resolution TEM (HRTEM), field emission scanning electron microscope (FESEM), Fourier transform infrared spectroscopy (FTIR), and Thermogravimetric analysis (TGA). Optical activity of as synthesized products was characterized by UV-Vis spectrophotometer.

HH5.26
Gold/Palladium Nanoparticles in Flight Thermal Annealing. <u>Jose A. Flores</u>[1,3], S. Mejia-Rosales[1,3] and E. Perez-Tijerina[1,2,3]; [1]Laboratorio de Nanociencias, Facultad de Ciencias Físico-Matemáticas UANL, San Nicolás de los Garza CP66450, Nuevo León, Mexico; [2]Centro de Investigación en Materiales Avanzados (CIMAV), Parque de Investigación e Inovación Tecnológia, Nuevo León, Mexico; [3]Laboratorio de Nanotecnológia, Cento de Inovación, investigación y Desarollo en Ingenería y Tecnológia (CIIDIT), Parque de Investigación e Inovación Tecnológia, Nuevo León, Mexico.

Gold/Palladium nanoclusters were produced by inert-gas condensation using a DC-sputtering system. The deposition parameters were chosen such that the mean size of the clusters were ~ 5nm. In order to study the structural changes on the AuPd clusters as the temperature is increased along their flight to the substrate, we adapted the IGC technique adding a lineal heater; this in situ modification allows transferring thermal energy to the clusters before deposition. Theoretical studies have demonstrated a correlation between the energy per cluster and their final size and shape; for this reason we produced the particles at several in-flight temperatures in a range that goes from room temperature to 1273 K. HR-TEM micrographs indicate that both morphology and structure of the cluster distribution have marked changes as a function of the on flight temperature.

SESSION HH6: Nanoparticles II
Chair: Valeri Petkov
Thursday Morning, April 16, 2009
Room 3009 (Moscone West)

8:30 AM *HH6.1
Small-angle X-ray and Neutron Scattering Measurements for Nanoparticle Size Evolution and Structure Using an In-Situ Reaction Flow Cell. <u>Andrew J. Allen</u> and Vincent A Hackley; Ceramics Division, NIST, Gaithersburg, Maryland.

The use of small-angle X-ray and neutron scattering (SAXS and SANS) methods has become widespread for quantifying nanoscale features in material systems of all types. The primary parameters obtained are the mean size, the total surface area and, with absolute intensity calibration, the volume fraction. However, the profile of the small-angle scattering as a function of the scattering angle (or momentum transfer, Q), being effectively a Fourier transform of the scattering morphology, generally contains much more detailed information than just these three parameters. With increasingly available high-brilliance X-ray synchrotrons and high-intensity neutron sources, it is becoming common practice to determine complete size distributions or fractal scaling laws, surface structure/roughness, and even anisotropic particle orientation distributions or shapes. The development of ultrasmall-angle scattering (USAXS and USANS) methods, which exploit crystal diffraction optics to extend measurements to smaller angles and correspondingly larger size, now allows the structure parameters to be determined over a contiguous length scale from nanometers to micrometers. Thus, agglomeration effects, and other scale-dependent features that connect nanoscales to mesoscales, can be quantified. For particulate systems, a remote-controlled, isothermal, circulating fluid flow cell offers further advantages: fluid flow prevents settling out of coarse particulates from suspension, and control and online monitoring of flow rate, temperature, and suspension conditions such as pH, permit real-time studies of solution-mediated processes over several hours. When used in SAXS or SANS studies, one can measure, in situ and in real time, structural parameters in the scale range from one nanometer to several micrometers in a system evolving in response to changing physical and chemical conditions. Furthermore, by using different solvents (or by exploiting the neutron isotope effect with H2O/D2O exchange in SANS) while maintaining a good absolute intensity calibration, information can be inferred about the inner structure (density, permeability, etc.) of the particles, themselves. Solution-mediated reaction routes are increasingly being exploited for the formation of non-agglomerated and mono-dispersed nano-scale particle systems. To gain insights into such processes, SAXS and SANS using a flow cell can provide representative and quantitative microstructure characterization, for example, of a nucleating solid phase from solution. This paper will illustrate these points with studies of carbon nanotubes and ceria nanoparticle formation from solution and show how SANS and SAXS can complement total scattering methods for investigating nanostructure. A.J. Allen, V.A. Hackley, P.R. Jemian, J. Ilavsky, J.M. Raitano & S-W. Chan; "In situ ultra-small-angle X-ray scattering study of the solution-mediated formation and growth of nanocrystalline ceria," J. Appl. Cryst., 41, 918-929 (2008).

9:00 AM HH6.2
EELS and STM/STS Measurements on Nitrogen Doped Single-walled Nanotubes: Towards Knowledge of Nitrogen Atomic Configuration in the C Network. <u>Raul Arenal</u>[1], Hong Lin[1,2], Jerome Lagoute[2], Odile Stephan[3], Sylvie Rousset[2] and Annick Loiseau[1]; [1]LEM, CNRS-ONERA, Chatillon, France; [2]MPQ, CNRS-U. Paris VII, Paris, France; [3]LPS, CNRS-U. Paris XI,

Orsay, France.

Nitrogen doped carbon nanotubes (CNx-NTs) are very interesting materials, since the incorporation of nitrogen atoms into the carbon network permits to tailor the electronic properties of the undoped C-NTs. Recently we have successfully synthesized single-walled (SW) CNx-NTs by vaporizing a C:Ni/Y target using a CO_2 continuous laser under a nitrogen atmosphere [1]. We have combined electron energy loss spectroscopy (EELS) and scanning tunneling microscopy (STM) and spectroscopy (STS) to determine the concentration and the atomic configuration of N atoms into the C network and their impact on the electronic structure of the tube. EELS in a dedicated scanning transmission electron microscope (STEM) is a crucial technique to perform nano-scale structural and chemical composition studies of materials, which greatly contributes to an improved understanding of their properties. In this communication we present our recent EELS studies on the synthesized CNx-SWNTs. We have therefore measured that the content of nitrogen in individual SWNTs as well as in bundles SWNTs is around 1.5 at.% [2]. Moreover, from the analysis of the fine structures near absorption edges (ELNES) we have deduced that N local environment is not always graphitic and can also correspond to the so-called pyridine-like configuration. STM and STS are also very appropriate techniques to investigate structural and electronic properties of NTs a nanometer scale. We will show in this communication how the different kinds of N environment can be identified and studied by these techniques. [1] H. Lin, J. Lagoute, C. Chacon, R. Arenal, O. Stephan, V. Repain, Y. Girard, S. Enouz, S. Rousset, A.Loiseau, Phys. Soli. Stat., in press (2008). [2] H. Lin, R. Arenal, S. Enouz-Vedenne, O. Stephan, J.L. Cochon, A.Loiseau, to be submitted (2008). Acknowledgements This work was supported by the European Commission under the 6 Framework Programme (STREP project BNC Tubes, contract number NMP4-CT-2006-03350.

9:15 AM HH6.3
Synthesis and Characterization of alpha-HgI(2) Nanoneedles. Edgar Mosquera-Vargas[1,2], Roberto A Palou[1,2], Willinton Farfan[1,2], Rajasekarakumar Vadapoo[1,2], Sridevi Krishnan[1,2] and Carlos Marin[1,2]; [1]Physics Department, University of Puerto Rico, San Juan, PR, Puerto Rico; [2]Institute for Functional Nanomaterials, University of Puerto Rico, San Juan, Puerto Rico.

Synthesis of one-dimensional α-HgI2 nanoneedles with stem diameter of 40 nm and lengths up to tens of micrometers, gradually becoming thinner to form a sharp tip have been reported for the first time. The morphology, nanostructure and chemical composition were characterized using techniques such as SEM, TEM, line EDS spectrum and high-resolution TEM, indicating that the nanoneedles were single crystalline with high purity and structurally uniform and dislocation-free. On the basis of a series of TEM observations, the nucleation and growth process of α-HgI2 nanoneedles could be interpreted. A model of the growth of α-HgI2 nanoneedles in Zeolite is proposed taking in account the diffusion-controlled growth theory.

9:30 AM HH6.4
Probing in situ the Molecules at the Surface of Nanoparticles by DOSY NMR Francois Ribot[1], Francois Guillemot[1], Benoit Dubertret[2], Luk van Lokeren[3] and Rudolph Willem[3]; [1]CMCP - UMR7574, UPMC / CNRS, Paris, France; [2]LPEM - UPR5, CNRS, Paris, France; [3]HNMR Centre, Vrije Universiteit Brussel, Toronto, Ontario, Canada.

Most of the nanoparticles (NPs), especially those prepared and handled as suspensions, are to be considered as hybrid systems. Indeed, the shell of capping molecules that usually covers their surface constitutes an important part and plays a key role on their behaviour. Accordingly, a detailed characterization of the interactions between organic molecules and NPs is highly desirable to understand and improve their syntheses as well as to rationalize their utilization in various applications. However, evaluating in situ the affinity of organic molecules for NPs is not a simple task, especially when the capping molecules are involved in a dynamic equilibrium between a free and a grafted form. DOSY (Diffusion Ordered Spectroscopy) is a technique based on pulsed field gradient NMR, which gives an elegant way to measure the diffusion coefficients. Species can thus be differentiated on the basis of their translational mobility and sorted according to their size, without the need of a physical separation. As a consequence, capping molecules interacting with NPs can be distinguished from the free ones as they diffuse more slowly. This technique has been used to investigate suspensions of titanium dioxide nanoparticles, prepared by hydrolysis-condensation of titanium butoxide in the presence of acetylacetone (acacH) and p-toluene sulfonic acid (pTsH) [1]. The use of DOSY NMR on CdSe quantum dots (QDs) stabilized by trioctylphosphine oxide (TOPO) and suspended in toluene has allowed to evidence the presence of free and adsorbed TOPO molecules, to quantify both species and to access the dynamic of their exchange process. A lifetime of ca 0.7 s has been measured for TOPO molecules interacting with CdSe QDs. 1. L. Van Lokeren, G. Maheut, F. Ribot, V. Escax, I. Verbruggen, C. Sanchez, J.C. Martins, M. Biesemans, R. Willem, Chem. Eur. J., 2007, 13, 6957.

9:45 AM HH6.5
Size, Stability and Chemistry of Nanomaterials and their Precursors by Mass Spectrometry Techniques. Jean Jacques Gaumet[1], Didier Arl[1], Stephane Dalmasso[2], Jean-Pierre Laurenti[2] and Frederic Aubriet[1]; [1]Laboratoire de Spectrométrie de Masse et de Chimie Laser, Paul Verlaine University - Metz, Metz, France; [2]Laboratoire de Physique des Milieux Denses, Paul Verlaine University - Metz, Metz, France.

The study of nanometer-sized cristallites provides an opportunity to observe the dependency between the size and the evolution of material properties, more specifically the transition from molecular to bulk-like behavior. Such materials can be prepared as dispersed colloids or trapped and stabilized within micelles, polymers, zeolites or glasses. Nanomaterials are also prepared as thin films generated either by laser ablation/desorption or metal organic chemical vapor deposition. Main techniques currently used to achieve their charaterization are physical and physico-chemical methods, such as Nuclear Magnetic Resonance (NMR), Transmission Electron Microscopy (TEM), X-ray diffraction and photoelectron spectroscopy, and optical spectroscopies. All these analytical tools are excellent for average analyses of clusters or nanomaterials. Moreover, interactions between atoms localized at the surface of (functionalized or not) nanoparticles and surrounding particles may occur and their sharp characterization is a

formidable challenge. Soft ionization mass spectrometry (MS) methods [Electro-Spray Ionisation - Fourier Transform Ion Cyclotronic Resonance MS (ESI-FTICRMS) and Matrix Assisted Laser Desorption Ionization coupled with Time of Flight MS (MALDI-TOFMS)] and associated fragmentation techniques appear to be an alternative way providing data on the size, stability and exact chemical composition of nanoparticles and their precursors, and potentially on interactions between particles. We report the application of both mass spectrometry techniques to analyze II-VI semiconductor nanomaterials (CdX with X = S or Se) generated by the thermal growing of organometallic precursors. ESI-MS was used for analyzing a specific cadmium thiophenolate complex which contained 17 cadmium atoms : $[(CH_3)_4N]_2[Cd_{17}S_4(SC_6H_5)_{28}]$. It showed a pseudomolecular ion at m/z 2548 with the formula $[Cd_{17}S_4(SC_6H_5)_{28}]^{2-}$ which confirms the quality of the synthesis. By MS/MS analysis (dissociation) of this ion, we concluded that there was a very stable neutral entity (Cd_4S_4) which appeared to be the elemental constituant of a II-VI nanomaterial core. This was confirmed with other metal thiophenolates. Various II-VI functionalized CdSe nanoparticles in the 1.5-5 nm diameter range generated by thermal growing were analyzed by MALDI-TOFMS. Mass spectra of these nanocrystals are consistent with TEM and optical spectroscopy measurements. The unique combination of MS techniques and physical methods brings new insight concerning the structure analysis, the stability and the chemical composition of these semiconductor nanomaterials. This approach will be extended to III-V materials in the future.

SESSION HH7: Interfaces I
Thursday Morning, April 16, 2009
Room 3009 (Moscone West)

10:30 AM *HH7.1
Characterization of Nanostructured Organic-Inorganic Hybrid Materials using Advanced Solid-State NMR Spectroscopy
Marek Pruski, Kanmi Mao, Jerzy W Wiench and Jennifer L Rapp; Ames Laboratory, Iowa State University, Ames, Iowa.

We demonstrate the applications of several novel techniques in solid-state nuclear magnetic resonance spectroscopy to the structural studies of mesoporous organic-inorganic hybrid catalytic materials. These latest capabilities of solid-state NMR were made possible by combining fast magic angle spinning (at 40-60 kHz) with new multiple RF pulse sequences. Remarkable sensitivity gain has been achieved in heteronuclear correlation (HETCOR) spectroscopy through the detection of high-γ (1H) rather than low-γ (e.g., 13C, 15N) nuclei. This so-called indirect detection method has been until recently impractical due to the lack of adequate 1H homonuclear decoupling schemes. The technique can yield through-space 2D 13C-1H HETCOR spectra of surface species under natural abundance within minutes, a result that earlier would have been considered unrealistic. The 15N-1H correlation spectra of species bound to a surface can be acquired, also without isotope enrichment. The first indirectly detected through-bond 2D 13C-1H and 13C-19F spectra of solid samples will be shown, as well. In the case of 1D and 2D 29Si NMR, the possibility of generating multiple Carr-Purcell-Meiboom-Gill echoes during data acquisition offered time savings by a factor of ten to one hundred. Examples of the studied materials include mesoporous silica nanoparticles functionalized with various types of organic groups, where solid-state NMR allows the definitive characterization. In particular, it can be used to (1) detail the structure of non-functionalized mesoporous nanoparticles, (2) study the structure and absolute/relative concentration of various moieties inside the mesopores, (3) determine their spatial distribution, orientation with respect to the surface and dynamic behavior, and (4) monitor the catalysts' stability under the reaction conditions.

11:00 AM HH7.2
Electron Microscopy and Raman Characterization of the Electron-Beam Irradiation Damage in Graphene and Graphene Multi-Layers. Desalegne Teweldebrhan[1] and Alexander A Balandin[1,2]; [1]Department of Electrical Engineering, University of California - Riverside, Riverside, California; [2]Department of Materials Science and Engineering, University of California - Riverside, Riverside, California.

Graphene, a planar single sheet of carbon atoms arranged in honeycomb lattice, has attracted major attention owing to a number of unique properties. Some of the most interesting characteristics of graphene are its extraordinary room temperature carrier mobility and recently discovered extremely high thermal conductivity [1]. The outstanding current and heat conduction properties are beneficial for the proposed electronic, interconnect and thermal management applications [2]. Graphene characterization and device fabrication require an extensive use of the scanning electron microscopy (SEM), transmission electron microscopy (TEM) and focused ion beam (FIB) processing. The techniques involving electron beam irradiation of samples may result in damage and disordering leading to deterioration of the electrical and heat conduction properties. The damage to the material, which consists only of a single or few atomic layers, during its characterization can be quite significant even at low radiation doses. In this talk we report micro-Raman investigation of changes in the single and bi-layer graphene crystal lattice induced by the low and medium energy electron-beam irradiation (5 - 20 keV) typical of the electron microscopy. The graphene samples have been produced by mechanical exfoliation from bulk graphite. The number of layers and their quality were verified with Raman spectroscopy [3]. It was found that the radiation exposure of graphene results in appearance of the strong disorder D band suggesting significant damage to the crystal lattice. The D and G peak evolution with the increasing radiation dose follows the amorphization trajectory, which indicates graphene transformation to nanocrystalline form, and then to amorphous carbon. The micro-Raman spectroscopy data for the transformation of graphene lattice was independently confirmed with the measurements of the electrical resistance of graphene samples. Using the Tuinstra - Koening relation for the intensity of the D and G peaks we were able to determine that the grain size in graphene is on the order of ~ 2.4 - 3.5 nm after few minutes of irradiation when graphene transforms to nanocrystalline form. The obtained results have important implications for graphene electron microscopy characterization and graphene device fabrication, which required electron microscopy and focused ion beam processing. The work in Balandin group was supported, in part, by DARPA - SRC Focus Center Research Program (FCRP) through the Interconnect Focus Center (IFC). [1] A.A. Balandin, et al., "Superior thermal conductivity of single-layer graphene," Nano Letters, 8, 902 (2008). [2] Q. Shao, G. Liu, D. Teweldebrhan and A.A. Balandin, "High-temperature quenching of electrical resistance in graphene interconnects," Appl. Phys.

Lett., 92, 202108 (2008). [3] I. Calizo, W. Bao, F. Miao, C.N. Lau and A.A. Balandin "The effect of substrates on the Raman spectrum of graphene," Appl. Phys. Lett., 91, 201904 (2007).

11:15 AM HH7.3
Using Multilayer Thin Films to Quantitatively Characterize Interfacial Reactions in Metal Hydride Material Systems at Sub-nanometer Length Scales. Stephen T. Kelly, Erkan Senses and B. M Clemens; Materials Science and Engineering, Stanford University, Stanford, California.

As nanostructured materials become more common interfacial reactions will play an increasingly important role in a wide variety of applications as the fraction of atoms at a surface or interface increases dramatically when critical dimensions are on the nanometer scale. In order to engineer materials with the desired properties a fundamental understanding of interfacial reactions is crucial. Multilayer thin films provide a unique platform for investigating interfacial reactions due to the potential for very high interface density and the one-dimensionality of the interfacial reactions. When combined with x-ray diffraction and x-ray reflectivity multilayer thin films can be used to quantitatively characterize interfacial reactions with precision better than 1 nm. We used this technique to examine interfacial reactions in two complex metal hydride materials with potential as practical on-board reversible hydrogen storage materials. We examined films with alternating layers of Mg and Mg_2Si as well as films with alternating Mg and Al layers in order to probe the hydride formation kinetics for the respective systems. Both the MgH_2 + Si and the $Mg(AlH_4)_2$ hydride systems suffer from practical limitations due to kinetic obstacles in the hydride formation reaction. These studies demonstrate the effectiveness and sensitivity of the combined multilayer and x-ray analysis technique in examining interfacial reactions at the nanoscale.

11:30 AM HH7.4
Ex situ Structural Characterisation of Interfaces in Epitaxial Fe/MgO/Fe Magnetic Tunnel Junctions. Chao Wang[1], Amit Kohn[1], Shouguo Wang[3], Amanda K Petford-Long[4], Lan Y Chang[1], Angus I Kirkland[1] and Roger C. C Ward[2]; [1]Materials, Oxford University, Oxford, United Kingdom; [2]Clarendon Laboratory, Department of Physics,, Oxford University, Oxford, United Kingdom; [3]State Key Laboratory of Magnetism,, Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing, China; [4]Materials Science Division,, Argonne National Laboratory, Argonne, Illinois.

Theoretical calculations of ideal epitaxial Fe (001)||MgO (001)||Fe (001) magnetic tunnel junctions (MTJ) predict tunnel magnetoresistance (TMR) ratios greater than 1000%1, 2. Although large TMR ratios were indeed achieved experimentally by some groups3-6, these values are still considerably lower than these theoretical predictions. In this work, we report on a detailed ex situ structural characterisation of such a device5, 6 using transmission electron microscopy (TEM). Our aim was to study the structural reasons for the discrepancy between the theoretical assumptions and the actual structure of epitaxial MTJ that demonstrate among the highest TMR ratios to date. In particular, we focused on the structure of the Fe/MgO interfaces, which are expected to influence significantly the TMR7-9. The atomic arrangement at the interface, namely how the Fe atomic columns are positioned with respect to the Mg or O atomic columns, was determined by Z-contrast scanning TEM (STEM) images. The results show that Fe columns are positioned on top of O columns in agreement with previous in situ low energy electron diffraction measurements10, thus confirming the structure used in the theoretical models. Calculations also demonstrate that the TMR ratio is reduced if the Fe/MgO interface is oxidized7, 8. By comparing experimental high resolution Cs-corrected TEM images with simulated images, and measuring the interplanar distances between Fe and MgO layers, we conclude that for the growth conditions used in this research, the interfaces are mostly sharp or un-oxidized. However, as opposed to the ideal model, the crystal structures of the layers are relaxed resulting in semi-coherent interfaces. Finally, the influence of the growth modes on the interface structure was characterized. Z-contrast STEM images and electron energy loss spectroscopy demonstrate that the bottom Fe/MgO interface is smoother than the top one. The reasons for the differences between the ideal and actual structures are discussed with respect to the growth parameters, lattice mismatch and surface energy of these films. 1 W. H. Butler, X.-G. Zhang, and T. C. Schulthess, Phys. Rev. B 63, 054416 (2001). 2 J. Mathon and A. Umerski, Phys. Rev. B 63, 220403 (2001). 3 S. Yuasa, T. Nagahama, A. Fukushima, Y. Suzuki, and K. Ando, Nature Mater. 3, 868 (2004). 4 C. Tiusan J. Faure-Vincent, C. Bellouard, M. Hehn, E. Jouguelet, and A. Schuhl, Phys. Rev. Lett. 93, 106602 (2004). 5 S. G. Wang, R. C. C. Ward, G. X. Du, X. F. Han, C. Wang, and A. Kohn, IEEE Magn. Trans. 44, Issue 11, xxxx (2008). 6 S. G. Wang, R. C. C. Ward, G.. X. Du, X. F. Han, C. Wang, and A. Kohn, Phys. Rev. B: Rapid Communications, accepted. 7 J. Mathon and and A. Umerski, Phys. Rev. B 74, 140404 (2006). 8 X.-G. Zhang, W. H. Butler, and A. Bandyopadhyay, Phys. Rev. B 68, 092402 (2003) 9 P. Bose, A. Ernst, I. Mertig, and J. Henk, Phys. Rev. B 78, 092403 (2008). 10 T. Urano and T. Kanaji, J. Phys. Soc. Japan 57, 3043 (1988).

11:45 AM HH7.5
Direct Probing of Nanocluster Interface Chemistry and Electronic Structure with Atomic Resolution. Shankar Sivaramakrishnan[1,2], Jianguo Wen[2], Benjamin J Pierce[1,2], Michael E Scarpelli[1,2] and Jian-Min Zuo[1,2]; [1]Materials Science and Engineering, University of Illinois, Urbana Champaign, Urbana, Illinois; [2]Fredrick Seitz Materials Research Laboratory, University of Illinois, Urbana Champaign, Urbana, Illinois.

Supported nanoclusters form the basis of many materials systems including catalysts, nanoscale electronic devices etc. A model system consists of a metal nanoparticle supported on a well defined facet of a semiconductor or an oxide. The interface plays a definitive role in determining the chemistry and electronic structure of the system. For example, charge transfer and band bending are two commonly identified phenomena with nanocluster interfaces. Conventional probes, such as X-Ray Photoelectron Spectroscopy (XPS), rely on data collected from an assembly of clusters and therefore average out nano-scopic phenomena. Weak effects at the interfaces of small clusters get buried in the signal from bigger clusters. In order to advance the science of

nanocluster interfaces, a local probe that can be applied to individual clusters is needed. In this work, we describe a technique to repeatedly probe individual nanocluster interfaces using Electron Energy Loss Spectroscopy (EELS) in an aberration corrected microscope. A unique sample preparation technique allows us to align the nanocluster interface parallel to the electron beam for model metal particles on semiconducting TiO2 oxide. We show results about interfacial structure, electronic structure and substrate strain caused by the interface obtained from supported Au nanoclusters, a famous model system to catalyze the conversion of carbon monoxide to carbon dioxide. We will discuss the results related to the origin of unusual chemical activity of this system, which has been a subject of hot debate.

SESSION HH8: Interfaces II
Thursday Afternoon, April 16, 2009
Room 3009 (Moscone West)

1:30 PM *HH8.1
Direct X-ray Determination of Structure, Composition and Strain in Epitaxial Nanostructures. Roy Clarke[1,2], Divine P Kumah[2], Codrin N Cionca[1], Joanna M Millunchick[3,2], Jenny Y Lee[3], Philip R Willmott[4], Christian M Schlepuetz[4], Stephan Pauli[4], Naji S Husseini[2], Rachel S Goldman[3,1,2], Leon A Webster[3,2], Jia-Hung Wu[3] and Yizhak Yacoby[5]; [1]Physics Department, University of Michigan, Ann Arbor, Michigan; [2]Applied Physics Program, University of Michigan, Ann Arbor, Michigan; [3]Materials Science and Engineering Department, University of Michigan, Ann Arbor, Michigan; [4]Swiss Light Source, Paul Scherrer Institut, Villigen, Switzerland; [5]Racah Institute of Physics, Hebrew University, Jerusalem, Israel.

Quantitative characterization of epitaxial nanostructures requires three-dimensional (3D) mapping with atomic resolution. Multiple complementary techniques are usually required, including high-resolution transmission electron microscopy, cross-sectional scanning tunneling microscopy, and x-ray scattering. X-ray analysis has several major advantages: it is non-destructive, capable of sub-Angstrom resolution and, utilizing the tunability of synchrotron x-ray sources, can provide quantitative 3D chemical composition distributions. In general, this analysis is a formidable task because only the intensity is measured in conventional x-ray scattering experiments; the *phase* of the scattered x-ray is undetermined. This is the well known and ubiquitous phase problem. We report here on recent progress in providing a solution to this problem for characterizing epitaxial nanostructures and buried interfaces, materials that are widely used in electronic and optoelectronic device applications. The diffraction patterns of such structures exhibit ridges of x-ray intensity (Bragg rods) along the direction normal to the plane of the substrate. The continuous nature of the Bragg rod scattering can be exploited to determine the phase of the complex structure factor of the 3D system. In this way the complete heteroepitaxial system, including the surface nanostructure and its interface with the supporting substrate, can be determined directly by Fourier inversion without resorting to *a priori* modeling and structure refinement. This phase retrieval method, Coherent Bragg Rod Analysis (COBRA), is applicable to any heteroepitaxial system that is in registry with the underlying substrate. We illustrate the approach with recent results on several epitaxial nanostructures of interest including complex oxide interfaces, compound semiconductor quantum dots and buried heterojunctions. The results provide insights on the essential microscopic details of the complex ionic and electronic reconstructions necessary to understand the intriguing physics exhibited by these materials.

2:00 PM HH8.2
X-Ray Diffraction and Raman Analysis of Thin Compressive Strained Epitaxial Germanium on Different Orientations of Silicon. Gaurav Thareja[1], Xiao Zhang[1], Szu-lin Cheng[2], Masaharu Kobayashi[1] and Yoshio Nishi[1]; [1]Electrical Engineering, Stanford University, Stanford, California; [2]Material Science and Engineering, Stanford University, Stanford, California.

Compressively strained epitaxial (epi) germanium (Ge) combined with double-gate (DG) Si-Ge-Si hetero-structure is a possible solution for MOS-FET with high mobility and low off-state leakage current [1]. An interesting challenge is to enable three dimensional vertical devices (Gate-All-Around (GAA), FINFET) with such hetero-structure setup. Vertical integration enables higher packing density and better electrostatic control of the gate around the channel. Thin film defect-free epi-Ge on different orientations of silicon (as in a silicon nano-pillar) combined with tunable value of compressive strain in Ge films, are some of the key issues that have been addressed in this work. Ultra-thin pseudomorphic Ge epitaxy is performed by Reduced Pressure Chemical Vapor Deposition (RP-CVD). We observe that low temperature (~310C) coupled with high germane partial pressure (~210 Torr) ensures low surface roughness (< 0.5 nm) epi-Ge films. Subsequent to Ge epitaxy, high resolution XRD using a hybrid monochromator is used to measure the strain for different thickness (3-8 nm) of germanium films on silicon. Using the XRD rocking curve (ω-2θ scan), compressive strain in Ge is indicated by a left peak shift from the reference theoretical relaxed Ge curve. Raman spectroscopy (514 nm laser) is performed and a blue shift in the Ge-Ge peak indicates compressive strain in Ge [2]. An average compressive strain of 1.5-2% is observed, which is less than the lattice mismatch of ~4% between Si and Ge. This is due to the defects at the Ge-Si interface and slight intermixing between Si and Ge both of which might have contributed to relax strain. Strain measurements in Ge are also performed on different orientations of silicon. All the information derived from the XRD and Raman measurements combined with careful TEM/SEM characterization is used to explain the SK growth mode of epi-Ge around Si nano-pillar (GAA) device. [1] T.Krishnamohan et al, IEEE Trans Elec. Dev., 53(5), 990-1009 (2006) [2] Tsang et al, App Phy Lett, 51(21), 1732-1734 (1987)

2:15 PM HH8.3
Evaluation of Nano-scale Quantum Devices Using X-Ray Diffraction and Fourier Analysis. Liwei Cheng[1], Ruth E Choa[2], Jacob B Khurgin[3], Fow-Sen Paul Choa[1], Jianxin Chen[4] and Claire Gmachl[4]; [1]CSEE, UMBC, Baltimore, Maryland; [2]Centennial High School, Ellicott City, Maryland; [3]ECE, JHU, Baltimore, Maryland; [4]EE, Princeton University, Baltimore, Maryland.

Nano-scale superlattice (SL) based devices like quantum well infrared detectors (QWIPs) and quantum cascade lasers (QCLs) have existed for more than a decade. However, until now, we have lacked a systematic methodology for studying and understanding the relationship between device performance and material quality. For example, interface and surface states affect interband devices significantly because their carrier lifetime is in the nanosecond to microsecond scale. On the other hand, it is not clear how hetero-interface states affect the performance of intersubband devices because their lifetime (of intersubband states) is in the picosecond to sub-picosecond range. In this work, we use X-ray diffraction techniques and Fourier analysis to study and compare MBE (at Princeton U.) and MOCVD (at UMBC) grown SLs and QCLs. X-Ray results of QCLs with the same structure but dramatically different device performances are compared and analyzed. Although this is not a comprehensive method for failure mode analysis of nano-scale devices, it does provide essential information on why one device outperforms another and how growth quality affects intersubband devices. X-ray diffraction patterns can be quantitatively described through Fourier analysis. In a 1-D superlattice, the gradual change of a superlattice period can be observed in the Fourier space as a reduction of the convolution length. The degradation of the superlattice periodicity eventually affects all the satellite peaks. Besides a reduction in the number of observable satellite peaks, the linewidth of each peak may also gradually broaden (seen especially in higher harmonic peaks). The asymmetry of the satellite peak envelope is related to the atomic scale lattice mismatch. There are several factors that affect the linewidth of each satellite peak each factor shows its individual characteristics in the diffraction pattern. Details of each broadening effect will be discussed. Interface imperfection can also be identified indirectly from an overall scan of the spectrum for satellite peak presence, where new peaks correspond to multiple times of the thickness of the original period will appear as a result of losing degeneracy. X-ray spectra of high power room temperature CW QCLs and X-ray scans from the same layer structure but with dramatically differing device performance will be compared. We will provide a detailed explanation on how and why device performance varies. Examples of X-ray scans showing hetero-interface problems will also be presented.

2:30 PM HH8.4
Backside Analysis of Ultra-Thin Film Stacks in Microelectronics Technology Using X-ray Photoelectron Spectroscopy
Thomas Hantschel, Cindy Demeulemeester, Arnaud Suderie, Thomas Lacave, Thierry Conard and Wilfried Vandervorst; IMEC, Leuven, Belgium.

The use of ultra-thin layers for high-k metal gates for improved transistor performance poses big metrology challenges as the total thickness of such stacks is only a few nanometers. The characterization of such stacks requires an analysis technique which is extremely surface sensitive and can provide information about the stack composition, interaction at the interfaces between the different layers and the influence of different processing steps on stack composition. X-ray photoelectron spectroscopy (XPS) is gaining increasing importance for this task in the last few years. As the analysis depth of XPS is however limited to about 5-7 nm, and to avoid perturbation of the XPS signal from top surface contamination, the possibility to perform the analysis also from the wafer backside is urgently needed in order to gain access to the region of interest. This requires the removal of hundreds of micrometers thick bulk silicon substrate and to stop at the same time at the layer of interest with nanometer-scale accuracy. To tackle this enormous challenge, we have developed dedicated sample preparation procedures and applied the backside XPS backside to different material systems. The key of the developed method is an optimized procedure for plan-parallel polishing and etching in combination with optical fringes for thickness measurement. In this paper, we are presenting for the first time results of optimized backside XPS sample preparation and demonstrate its potential to gain insight into the interactions of high-k layers during annealing steps. Silicon-on-Insulator (SOI) and common silicon wafers have been used. Using lapping and poslishing steps, the silicon thickness is reduced down to about a few hundreds of nanometers. We observed that the use optical fringes is very efficient to detect the polishing end point and that the use of a tool for plan-parallel polishing is essential to obtain good results.The remaining of the few hundreds of nanometer thick silicon are removed by a careful wet etching step whereby long overetching must be avoided. XPS mapping can then be used to locate the appropriate sample area and the XPS analysis is being carried out. We investigated high-k metal gate stacks consisting of TiN/Al2O3/HfO2/SiO2/Si before and after annealing. After annealing, a slight increase of the intensity around 458 eV Binding energy indicated the formation of an oxidized layer, likely from the oxidation of the interface between the Al2O3 and the TiN. This has been confirmed by X-ray reflectometry (XRR) analysis of the same samples. AFM measurements have been used to investigate the smoothness of the prepared films and are going to be discussed.

2:45 PM HH8.5
Experimental Analysis of Out-of-Plane Strain Neutrality in Multilayer Quantum Dot Embedded p/i/n Diodes. Chris Bailey, Eric K Albers, S. J Polly, D. V Forbes, Seth M Hubbard and Ryne P Raffaelle; NanoPower Research Labs, Rochester Institute of Technology, Rochester, New York.

High material quality in devices using epitaxially grown low dimensional structures is necessary for optimal performance in devices such as quantum dot (QD) solar cells, QD infrared photodetectors, and QD lasers. Epitaxial growth of semiconductor QDs utilizes the Stranski-Krastanov (SK) strain-induced growth mode. Strain within devices can reduce material quality and result in undesirable effects in performance. QD devices using this method of growth can suffer in performance due to non-radiative recombination and therefore result in unwanted increases in dark current. High dark currents in QD solar cells, in particular, lead to voltage losses that ultimately degrade efficiency. In order to enhance the absorption properties of a single junction p/i/n GaAs solar cell, InAs quantum dots (QD) have been grown in the intrinsic region by the SK growth usingorganometallic vapor phase epitaxy. The large compressive lattice constant mismatch of the InAs/GaAs system (7%) can cause misfit dislocations in the QD region and threading dislocations throughout subsequently grown material[1]. Due to its aggressive tensile mismatch to GaAs (3.6%), layers of GaP are used here to offset this strain (strain compensation). Four GaAs quantum dot diodes using varying strain compensation thicknesses were grown with 3, 5, 7 and 9 ML of GaP. High resolution x-ray diffraction (HRXRD) symmetric measurements are used to investigate the strain in the material. Using a kinematic approach, the strain was determined for each

sample. An out-of-plane strain neutral condition was approximated to occur with 5 ML of GaP by interpolation. The "zero-stress method," incorporating layer and host material stiffness coefficients, and lattice parameters was used to calculate an in-plane strain-neutral condition found to be 2 ML of GaP. Because the experimental x-ray scans indicate only out-of-plane strain, further verification of zero in-plane strain is still necessary. Since x-ray intensities can be overestimated when layers are thicker than one half of the extinction length, x-ray simulation of the layers is performed, using a semi-dynamical theory which approximates the QD layers as 2D thin films. Using this data, a strain-neutral condition is found to be 3 ML of GaP. Discrepancies between these values can be explained by the inconsistency of comparing out-of-plane and in-plane strain methods, and considering that the x-ray scans are of 3D structures, while the zero stress method and simulation assumes 2D films. Dark current measurements are taken for all of the diode samples, and the saturation currents are extracted. Saturation current was minimized in the 5 ML sample $J_0 = 2.60 \times 10\text{-}10$ mA/cm^2, indicating the highest quality material. This is in agreement with the HRXRD analysis.

Photoluminescence, TEM images, and spectral response are presented for further material quality analysis. 1. J T Ng et al 2007 Semicond. Sci. Technol. 22 80-85

3:30 PM *HH8.6
Combining Computation and Experiment to Probe Interfacial Chemistry at the Nanoscale. <u>Donald Siegel</u>[1], Aniruddha Biswas[2], David Seidman[2] and Chris Wolverton[2]; [1]Ford Motor Company, Dearborn, Michigan; [2]Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois.

One of the most commonly used techniques to increase the strength of metallic alloys is the precipitation of a second phase compound. This approach is widely employed to improve the mechanical properties Al alloys, and is of maximum benefit when the precipitates exhibit a high number density while maintaining nanometer-scale dimensions. Since the size and density of precipitates depends critically upon the energy of the matrix-precipitate interface γi, the ability to predict and optimize precipitation strengthening relies upon the accuracy with which γi can be determined or the degree to which it can be modified. At an elementary level, γi is controlled by the local structure and chemistry of an interfacial region typically only a few nanometers thick. Given the small scale and three-dimensional nature of these structures, elucidation of the nanoscale chemistry at matrix-precipitate interfaces has historically proven to be a highly non-trivial task. However, recent advances in experimental techniques (i.e., the local electrode atom probe) combined with first-principles computational modeling herald new opportunities for the characterization of interfacial properties. In this talk we demonstrate how such a combination of experimental and computational techniques has been applied to uncover the interfacial chemistry of precipitate-matrix interfaces in the compositionally-complex commercial Al alloy "319." For the first time, we reveal an anisotropic enrichment in solute concentration between the two classes of interfaces bounding the main strengthening precipitate θ′. Solute segregation at the rim of the precipitate, characterized by a semi-coherent interface with the Al matrix, is observed to be several times larger than at the broad, coherent interfaces. These results are consistent with the more open structure of the semi-coherent interface, which exhibits a much larger misfit & interfacial energy than the coherent interface. First-principles calculations are used to evaluate the thermodynamic factors underlying the solute enrichment, and are found to be in good agreement with the experimental data.

4:00 PM HH8.7
Assembling Monolayer Protected Gold Nanoparticles onto the Surface with an Orientation <u>Ying Hu</u>, Oktay Uzun, Cedric Dubois and Francesco Stellacci; Department of Materials Science and Englineering, MIT, Cambridge, Massachusetts.

Ying Hu, Oktay Uzun, Cedric Dubois, Francesco Stellacci Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA, 02139 Gold nanoparticles coated with a self-assembled monolayer (SAM) of thiolated molecules have been investigated as an important building material for nanometer sized electronic structures. In this talk we present a combined scanning tunneling microscopy (STM) and transmission electron microscopy (TEM) study of two types of equally monodisperse gold nanoparticles, one coated only with dodecanethiol ligands ("homoligand") and the other coated with a mixture of deodecanethiol and 4-methylbenzenethiol ligands. In our previous work, we demonstrated that for certain nanoparticles, specific mixed ligands will phase separate on top of the nanoparticles, forming ribbon-like domains of alternating composition ("rippled"). These structures have been demonstrated to have unique solubility and biofunctions, specifically it can transfer through the cell membrane without rupturing it. A comparative analysis shows that homoligand nanoparticles interdigitate less into one another than the rippled particles, and readily form hexagonally packed supracrystals while rippled particles are trapped in more disordered 'glassy' arrangements. Furthermore, we demonstrated a controlled method of assembling nanoparticles onto the metal surface with an orientation. The "rippled" nanoparticles have two diametrically opposed positions that are more kinetically active and can selectively react with MUA ligands. So by modifying the gold surface with 5-amino-2-mercaptobenzinidazole molecules that chemically react with MUA ligands, we can assemble the nanoparticles onto the gold surface with an orientation. The prepared surface was then studied with Scanning Tunneling Microscopy. For comparison, "rippled" nanoparticles were also randomly assembled onto the surface by drop-cast method. We observed significant differences between samples prepared by the pole-up method and the drop-cast method. On the pole-up sample, this phase separated structure can be observed only on a portion of the surface; the phase separated structure can be observed across the surface on samples prepared by the drop-cast method. The active sites on top of the nanoparticles assembled onto the surface by the pole-up method enable us to build further complicated multi-layer structures.

4:15 PM HH8.8
Composition Quantification of Microelectronics Multilayer Thin Films by EDX: Toward Small Scale Analysis. <u>Thierry Conard</u>[1], Kai Arstila[1], Thomas Hantschel[1], Wilfried Vandervorst[1,3], Emma Vecchio[1], Simon Burgess[2] and Frank Bauer[2]; [1]IMEC, Leuven, Belgium; [2]Oxford Instrument, Oxfordshire, United Kingdom; [3]KULeuven, Leuven, Belgium.

In order to continuously improve the performances of microelectronic devices through scaling, SiO_2 is being replaced by high-k materials as gate dielectric and metal gates are replacing poly-Si. This leads to complex stacks, including several layers with different roles such as capacitance improvement, workfunctions adjustments, passivation layer, … For future generation, the replacement of Si as a substrate by Ge and/or III/V material is also considered. A thorough characterization, including composition is thus needed. Many different techniques exist for composition analysis, such as XPS, AES, RBS, ERD, MEIS, ICP-MS , …. They usually require however large area for the analysis, complex instrumentation and can be time consuming. EDX, when coupled to SEM has the potential to allow fast analysis on small scale areas. This study will evaluate the possibilities of EDX for thin film analysis based on an intercomparison of composition analysis with different techniques. To allow the comparison, this study will be performed on blanket wafer and several systems will be considered. First, a two layer system consisting of Al_2O_3/GaAs and HfO_2/GaAs will be evaluated for dielectric films down to less than one nanometer. Results will be presented for thickness accuracy and repeatability and for detection limits. Further, full gate stack will be considered, including TiN or TaN as metal; Al_2O_3 or La_2O_3 as dielectric cap layer and HfO_2 as dielectric. On these full stacks, the influence of thermal processing will be investigated. Finally, composition analysis of $Ta_xC_yN_zO$ over a wide range of composition will be compared to composition determined by XPS, AES and ERD. The application to small area analysis will also be demonstrated for areas below the $1\mu m^2$

4:30 PM <u>HH8.9</u>
Abstract Withdrawn

4:45 PM <u>HH8.10</u>
Quantitative Characterization of the Interface Between a V2O3 Layer and Cu3Au (001) by Cs Corrected HREM. <u>Hector A Calderon</u>[1], Horst Niehus[2,4], Bert Freitag[3], Fernando Stavale[4] and Carlos Achete[4]; [1]Ciencia de Materiales, IPN, Mexico, DF, Mexico; [2]Institut für Physik, Humboldt Universität zu Berlin, Berlin 12489, Germany; [3]FEI Company, Eindhoven, Netherlands; [4]Div. Metrologia de Materiais (DIMAT), Inmetro, Xerem RJ, Rio de Janeiro, Brazil.

Vanadium oxides are materials of interest due to their electronic, magnetic and catalytic properties. In the case of V2O3 and Cu3Au, the interfacial bonding is rather difficult to describe by a particular chemical bonding state, since the two component materials have strongly different electronic structures. Clearly, investigation of the local region at such an interface becomes important. In the present case it has been possible to grow a two dimensional multilayer of V2O3 (0001, corundum structure) on top of the Cu3Au (001, L12 structure) substrate. High resolution images (HRTEM) without any aberration correction have strong limitations since they cannot be directly interpreted either for the true position of atoms nor for the nature of the atomic species. In this investigation, the incoherent interface between vanadium sesquioxide and a Cu3Au (001) substrate is described with the help of image corrected HRTEM and focal series reconstruction. Quantitative results can be shown for the chemical composition of columns and strains at the interface. A model of the interface can be constructed from the experimental observations.