Wednesday Morning, October 22, 2008

Nanometer-scale Science and Technology
Room: 311 - Session NS+NC-WeM

Characterization and Imaging of Nanostructures

Moderator: R. Ruiz, Hitachi Global Storage Technologies Inc

8:00am **NS+NC-WeM1 Peter Mark Memorial Award Lecture: Probing the Order Parameter Dynamics and Energy Dissipation on a Single Defect Level: Hidden Dimensions of Scanning Probe Microscopy**, ***S.V. Kalinin****, Oak Ridge National Laboratory **INVITED**

The kinetics and thermodynamics of first-order phase transitions and reactions involving solids are universally controlled by defects. Examples are as diversified as nucleation centers in solid-state and electrochemical reactions, phase change and electrochemical memories, crystallization of metals, oxides, and polymers. The electronic and atomic structure of defects in solids has become accessible in exquisite detail with the advent of electron microscopy and spectroscopy techniques. In the last decade, the progress in AFM- unfolding spectroscopy and IETS has opened the pathway for probing thermodynamics and kinetics of single-molecule reactions, and vibrational modes within simple molecules. In comparison, the role of defects in solids on local phase transitions and order parameter dynamics has long remained beyond the experimental reach. In this presentation, I will summarize recent progress in spectroscopic multidimensional SPM techniques as applied for probing structure-property relationships on a single defect level using electric or thermal field confinement by an SPM tip. Ferroelectric materials provide a convenient model system in which bias-induced phase transition between two equivalent polarization states is reversible and is not associated with diffusion, mass, or significant heat exchange and strain effects. Spatially resolved mapping of local nucleation biases allows nucleation centers to be visualized, and corresponding thermodynamic and kinetic parameters to be reconstructed. The hysteresis loop fine structure provides additional information on defect-mediated domain dynamics and defect-domain interactions. The direct imaging of a single nucleation center on sub-100 nanometer level is demonstrated. In the second part of the talk, I demonstrate the approach for dissipation probing in SPM using non-sinusoidal signals (band excitation method). In all these examples, the 3- and 4D SPM techniques enabled by the recent advances in fast data acquisition electronics are the enabling step. Finally, I discuss potential pathways for extending these concepts from observation to control and communication with the nanoscale world. Research was supported by the U.S. Department of Energy Office of Basic Energy Sciences Division of Materials Sciences and Engineering and was performed at Oak Ridge National Laboratory which is operated by UT-Battelle, LLC.

8:40am **NS+NC-WeM3 Quantitative Evaluation of Carbon Nano Tubes by the Scanning Atom Probe**, ***O. Nishikawa***, *M. Taniguchi*, Kanazawa Institute of Technology, Japan

Quality of carbon nanotubes (CNT) strongly depends on the amount of impurities such as hydrogen, oxygen and others. However, few efforts have been paid for the quantitative evaluation of them. In order to evaluate the CNT at the atomic level point of view we mass analyzed various CNTs such as single walled CNT (SWCNT), double walled CNT (DWCNT) and multi walled CNT (MWCNT) utilizing the unique capability of the scanning atom probe (SAP).[1] In this mass analysis carbon atoms of the CNTs are field evaporated as positive ions of single atoms and clusters of few atoms. The mass to charge ratios of these ions are obtained by measuring their flight times from a specimen surface to an ion detector. One of the analyzed SWCNTs is grown by the high CO pressure process (Hipco) and other is synthesized by a direct-current arc-discharge method in He gas with Fe/Ni/S catalysis. The DWCNTs are commercially supplied. The MWCNTs are directly formed on a substrate of Ni-Cr-Fe alloy by thermal CVD at 650° using a mixture of acetylene, hydrogen and argon gases. CNTs are deposited on a W tip by silver paste. The amount of impurities is evaluated by counting the number of cluster ions forming mass peaks. For example, the numbers of C and H atoms forming the mass peak of 150 CH_3 clusters ions are 150 and 450, respectively. The number of C, H, O and other atoms are counted for all major mass peaks. The numbers of H, O and Na atoms in a Hipco SWCNT 3.7 %, 2.6 % and 0.1 % of the total number of detected atoms, respectively. Similarly, the amounts of the impurities in the CVD SWCNTs are 9 % of H, 0.7 % of O and 0.19 % of Na. The commercial DWCNTs contain fairly large amount of impurities with 20 % of H and 1.9 % of O. The MWCNT also contains a significant amount of impurities, 27 % of H, 4 % of O and 0.4 % of Na. Even if specimens are prepared by the CNT formed by an identical preparation process, most specimens show a different mass spectrum with different amount of impurities. However, many Hipco SWCNT specimens exhibit a similar mass spectrum. The binding between C atoms forming CNTs also evaluated. The mass spectrum with a large number of C^{2+} and C^{+} indicates that the C-C bonds of the CNT is strong and uniform. The relation between the binding state and the impurity content of the analyzed CNT will be discussed.

[1] O. Nishikawa, Y. Ohtani, K. Maeda, M. Watanabe and K. Tanaka: Mater. Char., 44, 29 (2000).

9:00am **NS+NC-WeM4 AgCl Monolayers on Au(111): Novel, Ultra-stable and Atomically-flat Surfaces**, ***E.V. Iski***, *M. El-Kouedi, D.O. Bellisario, E.C.H. Sykes*, Tufts University

Underpotential deposition (UPD) is a useful way of depositing up to one monolayer of a metal onto a more noble metal. We used this technique to deposit Ag onto Au(111) with and without the presence of chloride. Electrochemical scanning tunneling microscopy (EC-STM) revealed that, depending on the sample potential and hence the surface Ag coverage, Ag grows in a variety of ordered structures that can be atomically resolved. However, upon being removed from the electrochemical cell, these "chloride-free" Ag monolayers are subject to degradation by air. Interestingly, if the Ag layer is formed in the presence of trace amounts of chloride, the resulting AgCl layer is stable both in air and even at temperatures as high as 1000 K. X-ray photoelectron spectroscopy (XPS) was used to quantify the stoichiometry of the systems and both ambient- and EC-STM revealed that even after exposure to extreme temperatures the monolayer thick AgCl layer remained atomically perfect.

9:20am **NS+NC-WeM5 Atomic Scale Characterization of Charge Redistribution for Gallium Nanocluster Arrays on the Si(111)-7x7 Surface**, ***Q.H. Wang***, *M.C. Hersam*, Northwestern University

In recent years, the fabrication and characterization of nanocrystals with size-dependent properties has gained interest for both fundamental studies and technological applications ranging from magnetic storage to catalysis. Self-assembled arrays of uniform nanoclusters on the Si(111)-7x7 surface from In, Ga, and Al[1] have recently been observed. These nanoclusters share common characteristics: uniform atomic structure; high thermal stability; and self-assembly into well-ordered, large-area arrays. However, the electronic properties of these nanocluster arrays are not yet well understood. Experimental investigations thus far have focused on the behavior of individual nanoclusters rather than the delocalized properties of the nanocluster array as a whole. Meanwhile, a computational study of In and Al nanocluster arrays has predicted the formation of a spatially modulated 2D electron gas (2DEG) due to surface charge redistribution.[2] In this study, we report the observation of atomically resolved, delocalized 2D charge redistribution associated with Ga nanocluster arrays on the Si(111)-7x7 surface.[3] By using ultra-high vacuum scanning tunneling microscopy and differential tunneling conductance mapping, we correlate the topography of the Ga nanocluster array with its local density of states (LDOS). In the differential tunneling conductance maps, we observe the surface charge redistribution as distinct regions of increased LDOS forming an interconnected 2D network over the Ga nanocluster array. These results indicate that a delocalized 2DEG has been induced by the Ga nanocluster array. Furthermore, the close integration of the nanoclusters with the Si substrate can be discerned from differences in the LDOS between the faulted and unfaulted unit cell halves. Interestingly, the increased LDOS disappears abruptly over clean Si(111)-7x7 unit cells, suggesting a possible route for nanopatterning of the surface electronic structure via selective masking of the Ga nanocluster formation. These atomic-scale observations are likely to impact further fundamental studies of nanocluster arrays on Si and the development of potential nanoelectronic devices.

[1] J.F. Jia, X. Liu, et al., Phys. Rev. B, 66, 165412 (2002)
[2] L.X. Zhang, S.B. Zhang, et al., Phys. Rev. B, 72, 033315 (2005)
[3] Q.H. Wang and M.C. Hersam, Small, in press (2008).

9:40am **NS+NC-WeM6 QPlus AFM on Single Crystal Insulators with Small Oscillation Amplitudes at 5 K**, ***M. Maier***, Omicron NanoTechnology GmbH, Germany

The creation and investigation of nano-structures, molecules or atomic structures on insulating surfaces is a key approach for electronic decoupling from the substrate. It pushes AFM as an complementary imaging and spectroscopy technique to STM. Ideally, the used AFM probe should simultaneously or alternatively work in STM/STS modes without performance compromises on the latter. Based on a proven low temperature (5K) LT STM platform, we have integrated a QPlus[1] sensor, which employs a quartz tuning fork for force detection in non-contact AFM. For combined

***** Peter Mark Memorial Award Winner

STM operation, this sensor has key advantages over conventional cantilevers: (i) a solid metal tip for optimal STM/STS and (ii) high stiffness and high stability, i.e. low vibrational noise due to small self-resonance amplitudes. For quantitative force spectroscopy on insulating thin films or semiconductors, decoupling of tunneling current and piezo-electrically induced AFM signal is important. By measurements on Si(111) and Au(111) we prove that only a dedicated pre-amplification technique can solve this problem. In addition, extremely low signals require the first amplification stage to be very close to the sensor, i.e. to be compatible with low temperatures. STS measurements using a Niobium tunneling tip reveal the superconducting gap with a FWHM of approx. 2.5 meV and prove a probe temperature of approx. 5K. The high stiffness (1800 N/m) of the sensor allows for operation with extremely small amplitudes to (i) more precisely keep the sensor with a certain force interaction regime, (ii) increase sensitivity especially for short range forces and (iii) allow for force measurements during atom manipulation experiments without disturbing the manipulation event as such.[2] As benchmark measurement, we present atomic resolution imaging on single crystal NaCl with oscillation amplitudes down 100pm (peak-to-peak) in constant df imaging feedback. Optimal S/N ratio is achieved with a frequency noise down to 30mHz (peak-to-peak). We also present atomic resolution measurements on MgO(100), C60 molecules on Ag(111), and first evaluation measurements of the QPlus sensor in Kelvin Probe (KPM) mode operation.

[1] F. J. Giessibl, et al., Appl. Phys. Lett. 73, 3956 (1998)
[2] M. Ternes, et al., Science 319, 1066 (2008).

10:40am **NS+NC-WeM9 Nanoscale Characterization of Thin Film Coatings Using Annular Dark Field Scanning Transmission Electron Microscopy**, ***G. Acosta***, *R. Vanfleet, D. Allred, R. Turley*, Brigham Young University

When considering the optical performance of thin films in the Extreme Ultraviolet (EUV), developing an accurate physical description of a thin film coating is necessary to be able to successfully model optical performance. With the short wavelengths of the EUV, film interfaces and sample roughness warrant special attention and care. The surfaces of thin film samples are routinely measured by Atomic Force Microscopy, from which roughness can be determined. However, characterizing the quality of interfaces below the surface is much more challenging. In a recent study of scandium oxide thin films, High Resolution Transmission Electron Microscopy and Annular Dark Field Scanning Transmission Electron Microscopy (ADF STEM) were used to study the cross section of the samples. ADF STEM data analyzed along a path into the volume of the sample (normal to the interfaces) reveals information of sample density versus depth. This density-depth profile reflects the presence of subsurface film interfaces in the volume of the sample. Additionally, information from the ADF STEM profile can be used to gauge the roughness of the subsurface interfaces, which is used to refine the sample description during modeling. We believe this is the first use of ADF STEM in this capacity. This characterization technique may provide key insight to subsurface interface quality, which is particularly important when optimizing the performance of multilayer coatings in the EUV.

11:00am **NS+NC-WeM10 Electron Structure of InGaAs/GaAs Quantum Dots in Limit of Small Sizes**, *I. Filikhin, J. Nimmo, M.H. Wu,* ***B. Vlahovic***, North Carolina Central University

We model InGaAs/GaAs quantum heterostuctured objects, such as quantum dots (QD) and quantum rings (QR), in limit of small sizes. The electronic structure of these objects is restricted to a few electron and hole levels.[1] For QDs with small sizes, the effect of non-parabolicity of the conduction band becomes very important. In our model, this effect is taken into account using the Kane formula. In this study we apply an effective approach in which the combined effect of strains, piezoelectricity and interband interactions are simulated by an effective potential.[2] Based on our model, we performed an analysis of capacitance-gate-voltage data[1] and photoluminescence spectra for QDs, QRs and for double concentric QRs. We show that our approach reproduces both the few electron energy level spectra and the increase of the electron effective mass relative to the bulk value due to non-parabolicity. In this case the effective mass of excited states must be energy dependent and differs from the ground state value. Also, the non-parabolic effect visibly shifts the electron energy levels in comparison with parabolic models. We include heavy holes into the model of band structure using the effective potential approach. This model allows us to reproduce measured transition energies and Coulomb shifts for excitonic complexes (X-, X+, XX).[3] Ga and In material mixing in InGaAs/GaAs QD[4] is also taken into account in this study. We compare our results with those obtained by kp-calculations[5] and atomistic pseudopotential models.[3] We note that calculations that model QDs from first principles are of fundamental interest, but our effective potential method has strong application significance, which will be appreciated by industry, due to its efficiency and accuracy in calculating physical properties. This work is supported by the DoD: W911NF-05-1-0502.

[1] B. T. Miller, et al. Phys. Rev. B 56, 6764 (1997); R.J. Warburton, et al. Phys. Rev. B 58, 16221 (1998); A. Lorke, et al. Phys. Rev. Lett. 84, 2223 (2000).
[2] I. Filikhin, et al. Phys. Rev. B 73, 205332 (2006).
[3] S. Rodt, et al. Phys. Rev. B 71, 155325 (2005); G. Narvaez et al. Phys. Rev. B 72, 245318 (2005).
[4] I. Kegel, et al. Phys. Rev. Lett. 85, 1694 (2000).
[5] J. I. Climente, et al., J. Phys.:Condens. Matter 17, 1573, (2005); A. Schliwa, et al., Phys. Rev. 76, 205324 (2007).

11:20am **NS+NC-WeM11 Characterization of Graphitic Coated Magnetic Nanoparticles used in Cancer Therapy**, ***S. Trigwell***, ASRC Aerospace, *A.S. Biris, Y. Xu, Z. Li, M. Mahmood*, University of Arkansas at Little Rock, *T.S. Nunney*, Thermo Fisher Scientific, UK

Graphitic carbon coated ferromagnetic nanoparticles of Co and Co/Fe with diameters of approximately 7 nm and cubic crystalline structures were synthesized by catalytic chemical vapor deposition (CCVD). X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) analysis indicated that the metallic nanostructures inside the carbon shells were preserved in the metallic state and were not oxidized, which made them excellent candidates for electromagnetic radiation absorbers for biological thermal applications. Confocal microscope images revealed effective penetrations of the nanoparticles through plasmatic membranes into cultured HeLa cancerous cells both in the cytoplasm as well as the nucleus. Low RF radiation of 350 kHz triggered the cell death, a process that was application time and nanoparticle concentration dependant. Compared to nanostructures such as single wall carbon nanotubes, magnetic nanoparticles demonstrated higher specificity for RF absorption and heating.

11:40am **NS+NC-WeM12 Towards Automation in the Characterization of Nanostructured Materials and Devices**, *U. Schmidt, T. Dieing, M. Kress,* ***K. Weishaupt***, WITec GmbH, Germany

The characterization of nanostructured materials implies knowledge about their chemical and structural properties, leading to a growing demand for characterization methods for heterogeneous materials on the nanometer scale. However, certain properties are difficult to study with conventional characterization techniques due to either limited resolution or the inability to chemically differentiate materials without inflicting damage or using invasive techniques such as staining. By combining various analytical techniques such as Raman spectroscopy, confocal microscopy and AFM in one instrument, the same sample area can be analyzed with all implemented methods, leading to a better understanding of nanostructured materials. Raman spectroscopy, a chemical analysis technique, combined with confocal microscopy enables the unique Raman imaging of heterogeneous materials. The power of Raman imaging stems from the high chemical information content of molecular vibrational spectra. In the Raman spectral imaging mode, a complete Raman spectrum is recorded at every image pixel, leading to a two-dimensional array consisting of ten-thousands of complete Raman spectra. From this array images are extracted by analyzing various spectral features (sum, peak position, peak width, etc). Differences in chemical composition, although completely invisible in optical images, will be apparent in the Raman image and can be analyzed with a lateral resolution down to 200 nm. If higher resolution is required, by simply turning the microscope turret, the confocal Raman microscope can be transformed in to an AFM. Using this imaging technique, structures below the diffraction limit can be visualized from the same sample area. For the analysis of various devices formed on a support, an automated sample positioner with a travel accuracy better than 5 µm is incorporated in the instrument. Special scripting functions allow the automated execution of predefined measurement sequences on any user defined selection of measurement points on the sample, guaranteeing the most comprehensive surface analysis tool for systematic and routine research tasks.

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