

Nanometer-scale Science and Technology Room 2016 - Session NS-MoA

Nanoscale Structures and Characterization I

Moderator: J. Wendelken, Oak Ridge National Laboratory

2:00pm NS-MoA1 Induced Water Condensation and Bridge Formation by Electric Fields in Atomic Force Microscopy, G.M. Sacha, A. Verdaguer, M. Salmeron, Lawrence Berkeley National Laboratory

The formation of nanometer-sized water bridges between an Atomic Force Microscope (AFM) tip and a sample is a phenomenon that has produced a great interest in the last years. New applications in imaging and nanofabrication have driven efforts to understand nanometer-size capillarity. Water bridges play also an important role in contacts between objects, where it affects friction and energy dissipation. The interest in the topic has spurred theoretical efforts to model different aspects of capillarity meniscus formation. Most models are based on macroscopic approximations, molecular level grand canonical Monte Carlo Simulations and Density Functional Theory, all of them involving substantial computational effort. We have developed a simple analytical expression that can be used to determine in a quantitative way the presence and shape of the water film that forms between tip and sample in humid environments. This film grows under the influence of the electric field forming a meniscus that becomes unstable when a critical field is reached, at which point it suddenly forms a bridge between tip and surface. In AFM the capillary force bends the lever, which for small spring constants can bring the tip in contact with the surface. This is observed experimentally as a sudden jump-to-contact. Our approximation allows us to determine the distance and the voltage at which this capillary jump takes place. Apart from providing a simple way to calculate the critical field and distance it improves our understanding of the mechanisms of water induced jump-to-contact. Understanding and predicting water bridge formation is important for many applications and has implications in other physical processes including friction and adhesion in humid environments. @FootnoteText@ @footnote 1@ Gomez-MoAivas, S.; SÄienz, J.J.; Calleja, M. and Garcia, R. Phys. Rev. Lett. 2003, 91, 56101. @footnote 2@ Paramonov P. V. and Lyuksyutov S. F. J. Chem. Phys. 2005, 123, 084705.

2:20pm NS-MoA2 Carbon Nanosheets, a Novel, Free-Standing, Two-Dimensional Carbon Nanostructure, B.C. Holloway, J.J. Wang, R.A. Outlaw, X. Zhao, M. Zhu, P. Miraldo, S. Wang, K. Hou, College of William & Mary

This presentation summarizes our work on the synthesis and characterization of a new, free-standing, 2-D carbon nanostructure, carbon nanosheets, on a variety of substrates including metals, semiconductors, and insulators by RF plasma-enhanced chemical vapor deposition. SEM, TEM, SAED, Raman, XPS, AES, FTIR, and XRD all indicate that carbon nanosheets deposit as smooth graphite sheets which are up to 8 microns in height but are 1 nm or less in thickness. Such nanosheets consist of, at most, a few graphene layers. The nanosheets stand off the growth substrate in a manner similar to aligned nanotubes grown by chemical vapor deposition. However, in contrast to CVD nanotubes, nanosheets do not require a catalyst for growth and can be patterned after deposition using standard photolithography techniques. Results of thermodynamic modeling and parameter variations show that hydrogen etching promotes the formation of the atomically thin structures while the anisotropic dipole created in the graphene planes by the plasma sheath promotes the vertical orientation. Several applications which use the high surface area, vertical orientation, substrate flexibility and atomically sharp edges will also be outlined.

3:00pm NS-MoA4 Morphology Control of Ferromagnetic Core-Shell Nanoparticles Electrodeposited on H-terminated Si(100), L.Y. Zhao, N. Panjwani, T. Chan, N. Heinig, K.T. Leung, University of Waterloo, Canada

Our recent work on metal nanoparticles (Cu, Ni, Co) electrochemically deposited on an ultrathin polypyrrole film grown on a gold-coated silicon electrode shows that the morphology (size, shape, density and distribution) of these nanostructured materials can be easily controlled by varying the wet deposition conditions (pH, electrolyte concentration, deposition potential, charge, and current density), and the thickness and morphology of the polypyrrole film. Using similar electrochemical techniques and by manipulating the solution chemistry, we have recently obtained on a H-terminated Si(100) surface mono-sized, uniformly distributed Fe core-shell nanoparticles with several different morphologies: quantum dots of 4-10 nm in diameter, 30x120 nm "nano-rice", and 40-60 nm nanocubes. These

nanoparticles are found to consist primarily of a polycrystalline Fe metallic core and a mixed Fe oxides shell (of several nm thick) and all exhibit interesting magnetic properties. In the present work, we illustrate that morphological changes can be induced by controlling the substrate conditions, solution parameters and an external magnetic field.

3:20pm NS-MoA5 Boron-based Nanostructures for High Temperature Energy Conversion, T. Xu, The University of North Carolina at Charlotte

Thermoelectric (TE) materials with high figure-of-merit (ZT) are of fundamental and practical interest for energy conversion. Low-dimensional nanoscale materials provide new possibilities to improve ZT based on quantum effects. The use of quantum dots, wires and wells as TE materials is an active area of study. However, most investigations focus on TE nanomaterials (e.g., Bi@sub 2@Te@sub 3@, Bi) for refrigerator (cooling) applications. We propose to study a new class of boron-based TE nanomaterials that will operate at high temperature, and be used for power generation. In this presentation, recent experimental results on synthesis of n-type boron-based TE one-dimensional nanostructures (i.e., CaB@sub 6@, SrB@sub 6@ and BaB@sub 6@ nanowires) will be reported. The nanostructures were synthesized by pyrolysis of diborane (B@sub 2@H@sub 6@) over certain metal oxide powders (e.g., calcium oxide (CaO) for synthesis of CaB@sub 6@) at elevated temperature and low pressure. The experiments were performed in a home-built low pressure chemical vapor deposition (LPCVD) system. Gold (Au), Nickel (Ni), Platinum (Pt) and Palladium (Pd) are effective catalytic materials for growth of aforementioned hexaboride TE nanostructures. The as-synthesized nanostructures were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and Raman spectroscopy. Possible mechanisms for the growth of these novel boron-based TE nanostructures will be presented. Combined with other properties of boron-based materials (e.g., low-density, superior mechanical properties, excellent thermal and chemical stability), these new TE nanostructures may find applications in the automotive industry and in high temperature micro- and nanoelectromechanical systems (MEMS and NEMS), electronics, and others.

3:40pm NS-MoA6 Plasmon Excitations in Metallic Nanoparticles Arranged in Crystalline Structures, H.J. Steffen, Steffen and Associates, Inc., Canada

The study of the character of collective electron density oscillations provides a fundamental understanding of the optoelectronic and photonic behavior of nanostructures. Consequently, electron-energy loss spectroscopy represents an important method for the structure analysis of materials with metallic nanoparticles since it contains valuable information about size, geometry and chemical composition of the particles and in addition, their spatial configuration, distance and crystalline order. Therefore, analytical model calculations and a parameter study were accomplished based on the hydrodynamic and density functional theory. Eigenfrequencies of plasmons were calculated and theoretical energy loss spectra were obtained by modelling the associated energy loss functions. Electron-energy losses appear at energies below 5 eV, far below the well-known dipole resonance energy of metallic spheres. The energy positions are dependent on the electron density, geometry, particle size, distance and crystalline structure of the particle arrangement.

4:00pm NS-MoA7 Growth of Tungsten Nanoripples Induced by Linearly Polarized Femtosecond Laser, H. Zhang, M. Tang, J. McCoy, T.H. Her, The University of North Carolina at Charlotte

Single-laser-beam induced nanoripples of tungsten is demonstrated in a laser-induced chemical vapor deposition (LCVD) system using tungsten hexacarbonyl as precursor and a linearly-polarized 400-nm femtosecond laser beam at 80MHz. The ripples have the shape of willow leaf with a long strip and two pointed ends, whose width is less than 100 nm and height on the order of 15 nm. The periodicity of the ripples is around 130 nm, which is about one third of the wavelength of the laser beam. The ripple orientation was found always parallel to the laser polarization, and hence can be controlled by changing the laser polarization direction. Different grating patterns were formed by scanning the laser beam along the substrate surface. Transverse pattern was formed when the scanning direction is perpendicular to the laser polarization, and longitudinal pattern was obtained when the scanning direction was parallel to the laser polarization. Effects of the laser power, exposure time, and scanning speed on the ripple formation were investigated. Different from the conventional laser-induced periodic surface structures (LIPSS)@footnote 1,2@ which can only occur by irradiating substrates near melting threshold, the tungsten nanoripples and gratings we report here can be heterogeneously deposited on a variety of substrates including insulators (glass, quartz, and sapphire

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etc.), wide band gap semiconductor (gallium nitride), and metals (gold, copper, and palladium etc.). Considering the simplicity of this process and material flexibility of CVD, our finding may provide a novel cost-effective patterning method to produce periodic subwavelength nanostructures of a wide range of materials. @FootnoteText@ @footnote 1@ Dieter Bäuerle, Laser processing and chemistry, 3rd. ed. (Springer, Berlin, 2000).@footnote 2@ J. E. Sipe, J. F. Young, J. S. Preston, and H. M. van Driel, Phys. Rev. B 27, 1141-1154 (1982).

4:20pm **NS-MoA8 Nanoscale Stepping Stones for Enhanced Charge Transport through Organic Materials**, *D.B. Robinson*, Sandia National Laboratories; *A.A. Talin*, Sandia National Laboratories, 94550; *R.J. Anderson*, Sandia National Laboratories

The charge transport properties of organic materials, and the mechanisms of this transport, depend strongly on the length scale being studied. At very short length scales, charge transport is sensitive to geometry, and experimental methods tend to be exotic and expensive, with low sample throughput. Among the most tractable device geometries that have been demonstrated is one consisting of an array or superlattice of particles spanning electrode pairs. We have developed a test platform for organic electronics based on this geometry that is especially simple, relying only on parallel, low-cost techniques including solution-based self assembly, and that is compatible with a range of characterization techniques such as cyclic voltammetry, surface-enhanced Raman spectroscopy, UV-visible reflectance spectroscopy, Auger electron spectroscopy, and electron microscopy. It is also compatible with architectures for sensing applications.@footnote 1@ For example, the in-plane conductivity through a thin film of a conducting polymer, poly (3-hexylthiophene), is enhanced by the presence of a regular array of metallic nanoparticles spaced on a length scale comparable to the persistence length of the polymer, perhaps because the particles provide resting points for charge carriers from which they can more easily proceed than they could from usual bulk trapping sites. Electrical properties are observed as a function of polymer molecular weight, particle type, and deposition method. @FootnoteText@ @footnote 1@ Wohltjen, H.; Snow, A.W. Anal. Chem. 70 947 (1998).

4:40pm **NS-MoA9 Partial Crystallization of HfO₂ and Its Application to Nanoscale Flash Memories**, *G. Zhang*, National University of Singapore; *W.J. Yoo*, Sungkyunkwan University, Korea, Singapore

The demands for non-volatile memories (NVM) in recent years have increased rapidly due to the growth of mobile device industries. Silicon-Oxide-Nitride-Oxide-Silicon (SONOS) type flash memory layer is extensively studied because of its potential as a high density memory. The high-k dielectric material HfO₂ is considered as a better trapping layer material than Si₃N₄ in SONOS because high k can provide better vertical scalability and data retention property. Amorphous HfO₂ crystallizes during high-temperature (> 650°C) treatments, which is a drawback of HfO₂ since the crystallization can induce high leakage current. According to the crystallization result obtained by X-Ray Diffraction (XRD), high intensity peaks of (-1 1 1) and (1 1 1) are observed after the thermal treatment for 5 s in the temperature range of 800°C - 1000°C. However, conducting-AFM topography image clearly shows that the crystallization across the HfO₂ film is non-uniform and the grains in the film are formed via partial crystallization. A two dimensional current image of C-AFM confirmed the non-uniform distribution of the grains, where leakage current is significantly higher than amorphous HfO₂. The z results (contrast in image) are 2nm for topography and 6 pA for current image. We consider that these grains act similarly to nanocrystal dots, which effectively suppress lateral charge migration under the programmed state, via charge localization inside the grains or at the grain boundaries. Excellent 2-bit/cell and 4-level/bit memory properties are achieved by Channel Hot Electron Injection (CHEI) program and outstanding charge retention property is achieved in both room temperature and at 85°C. The novel way of mimicking nanocrystal structure with partially crystallized continuous HfO₂ trapping layer easily enables multi-bit/cell operation and greatly extend the storage capacity of SONOS type flash memory.

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