

Wednesday Afternoon, October 17, 2007

Nanometer-scale Science and Technology

Room: 616 - Session NS2+EM-WeA

Nanoscale Devices and Nanowires II

Moderator: D.K. Ferry, Arizona State University, F.M. Ross, IBM T. J. Watson Research Center

1:40pm NS2+EM-WeA1 Real-time Studies of Metallic Nanodroplet Formation and Motion on Semiconductor Surfaces, *J.H. Wu, W. Ye, T. Sun, H.-Y. Chen, K. Thornton, R.S. Goldman*, University of Michigan

Arrays of metallic nanodroplets are of interest for a broad range of applications including magnetic memory arrays, plasmonic waveguides, nanowire growth seeds, and negative index of refraction materials. Although nanometer-sized metallic droplets often form on compound semiconductor surfaces during epitaxial growth, thermal annealing, and/or ion irradiation, the mechanisms of their formation are not well understood. In this work, we are examining the formation and motion of metallic droplets during ion-irradiation of a variety of semiconductor surfaces. We use real-time imaging in a dual-beam focused-ion-beam system followed by quantitative analysis of the instantaneous positions, sizes, and velocities of the droplets in each movie frame. On GaAs and GaSb surfaces, randomly distributed nearly pure liquid-like Ga droplets are observed to form above a critical dose. Subsequent ion beam irradiation results in growth, motion, and coalescence of the droplets. Since droplets are not observed on Si surfaces prepared under similar conditions, the droplet formation is likely associated with the preferential sputtering of group V elements and liberation of Ga from the substrate as it is milled. Under ion beam irradiation, Ga droplet motion is observed, possibly due to Marangoni motion, which is usually driven by a surface tension gradient. Since the Ga droplets are essentially liquid spheres, the weak atomic bonds and droplet shape lead to enhanced sputtering in comparison with the surrounding substrate. The enhanced sputtering at liquid droplets leads to both thermal and surface tension gradients between the droplets and the substrate, thus providing the driving force for droplet motion. Interestingly, a higher droplet velocity is observed on GaSb than on GaAs surfaces, suggesting that droplet motion is dependent on the energetics of the Ga-substrate interface. On GaAs surfaces, most droplets move in a direction opposite to the ion beam scanning direction, presumably due to the FIB-induced thermal gradient on the surface. In addition, the droplet velocity is size-dependent, with higher velocities for larger droplets, suggesting the thermal/surface tension gradients increase with droplet size. The velocity is apparently correlated with the rate of droplet size change, suggesting that a mass transfer/exchange process occurs during droplet motion. This phenomenon is less significant for droplets that have merged with other droplets.

2:00pm NS2+EM-WeA2 A Periodic Table of Silicon-Metal Nano-Templates for Cluster-Assembled Materials, *G.K. Gueorguiev, S. Stafström, L. Hultman*, Linköping University, Sweden

The structure and bonding properties of MSi_n clusters, containing 1 to 14 Si atoms together with one transition metal atom among 24 different elements: Cr, Mo, W, Mn, Tc, Re, Fe, Ru, Os, Co, Rh, Ir, Ti, Zr, Hf, V, Nb, Ta, Ni, Pd, Pt, Cu, Ag, Au, were studied by first-principles calculations. Some of these clusters are known to have been synthesized. The transition metal atoms work as nucleation sites for MSi_n . We find that species with $n = 3, 5, 7, 10, 12$ are stable and exhibit shapes independent on the metal atom involved which establishes a systematic behavior for MSi_n . For most metals, due to p-d orbital hybridization, both MSi_{12} and MSi_{10} (the smallest endohedral species) are highly symmetric, exhibiting the shapes of a hexagonal prism (D_{6h}) and of a bicapped tetragonal antiprism (D_{4d}), respectively. For such clusters, we predict similar packing rules, but considerably different electronic properties. Nano-wires (hexagonal nanocylinders) assembled from MSi_{12} are stable and with tunable electronic properties. These attributes suggest MSi_n as building blocks for cluster assembled materials. We have systematized the results on MSi_n by the organization of the transition metals in the Periodic Table.

2:20pm NS2+EM-WeA3 Sc Silicide Epitaxial Nanowires on Si(001): A Comparison with Rare Earth Silicide Nanowires, *J. Nogami, Y. Chai*, University of Toronto, Canada, *G. Ye, M.A. Crimp*, Michigan State University

Rare earth (RE) metals can form self-assembled silicide nanowires when grown epitaxially on Si(001) substrates. These nanowires form due to an anisotropy in lattice mismatch between the hexagonal form of the silicide

and substrate, with extended growth occurring along the direction of low mismatch.^{1,2} In this context, the growth of scandium silicides is interesting since Sc_3Si_5 has the same crystal structure as the RE silicides, but with the direction of close match along the c rather than the a axis. This raises the intriguing possibility of growing nanowires that are naturally perpendicular to RE silicide nanowires. The initial stages of Sc silicide growth on Si(001) was studied by scanning tunneling microscopy, transmission electron microscopy (TEM) and atomic force microscopy. The nanostructures can be divided into two classes: tabular rectangular islands with small aspect ratios, and highly elongated nanowires with triangular cross section. Surprisingly, there is no indication that the common growth direction of the nanowires is rotated with respect to RE nanowires. At the same time, TEM shows that the triangular nanowires have a two phase crystal structure, with a Sc rich silicide growing on top of a Si rich silicide. The differences in growth behavior with respect to the RE silicides will be explained in terms of the differences in stable silicide phases seen in the phase diagrams of these systems.

¹Y. Chen, D. A. A. Ohlberg, G. Medeiros-Ribeiro, Y. A. Chang, and R. S. Williams, Appl. Phys. Lett. 76, 4004 (2000).

²J. Nogami, B. Z. Liu, M. V. Katkov, C. Ohbuchi, and N. O. Birge, Phys.Rev.B 63, 233305 (2001).

2:40pm NS2+EM-WeA4 Time-resolved X-ray Excited Optical Luminescence Characterization of Si Nanowires*, *R.A. Rosenberg, G.K. Shenoy*, Argonne National Laboratory, *P.S.G. Kim, T.K. Sham*, University of Western Ontario, Canada

Due to quantum confinement effects nanostructures often exhibit unique and intriguing fluorescence behavior. X-ray excited optical luminescence (XEOL) provides the capability to chemically map the sites responsible for producing low energy (1-6 eV) fluorescence. By taking advantage of the time structure of the x-ray pulses at the Advanced Photon Source (APS, ~80 ps wide, 153 ns separation) it is also possible to determine the dynamic behavior of the states involved in the luminescence. In this presentation we show how this technique can be utilized to understand the XEOL from silicon nanowires (~50 nm diameter). Analysis of the XEOL spectra revealed the presence of three peaks at 475, 540, and 640 nm whose breadth increased with increasing wavelength. To gain insight into the dynamic nature of the luminescence, time-gated spectra were obtained as the x-ray energy was varied through the Si K edge. Data were obtained using 15-140 ns and a 0-10 ns gates. For the long time gate the areas are roughly evenly distributed among each of the peaks. However, in the short time gated data the 640 nm peak is dominant. This clearly demonstrates that the relative lifetime of this state is shorter than the other two. This is in contrast to the conventional wisdom for homo-structured and single component materials, for which the lifetime usually increases with wavelength. By extracting the intensity of each peak as the x-ray energy is scanned thru the Si K edge we are able to demonstrate that the 540 nm luminescence emanates from the Si nano crystallites imbedded in the wire, the 475 nm peak originates from the oxide shell, and the 640 nm peak comes from defects located near the Si-SiO interface.

*Use of the Advanced Photon Source was supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

3:00pm NS2+EM-WeA5 Enhancement of CHEI Programming Efficiency Using Extended SixZr1-xO2 Interface Formed by ZrO2 Charge Trapping Layer, *G. Zhang, W.J. Yoo*, Sungkyunkwan Advanced Institute of Nano-Technology, Korea

Channel hot electron injection (CHEI) programming is widely used for NOR Flash memory operations, whose efficiency is determined by both hot electron (HE) injection level and electron capture rate in which an electron excitation and relaxation process is involved.¹ Inelastic phonon scattering is considered as the main mechanism to cause HE relaxation, where HE energy loss rate decays with larger electron/phonon temperature divergence.² As a result, electron capture rate of deep traps decays sharply with the increase of HE temperature (T_e).³ We consider that phonon scattering occurs actively at interfacial junction of different layers, where regularity of lattice structure is disturbed. In this work, we investigated capture rate dependent CHEI programming efficiency for different junction widths or phonon temperatures (T_p). It is found that HEs are injected into the gate stack as lucky electrons,⁴ resulting in small capture rate or low programming efficiency; instead, warm electrons (WE), which are generated by thermally enhanced F-N tunneling, play a more important role in programming with higher capture rate. In this work, a practical method to effectively enhance programming speed using extended SixZr1-xO2 interfacial junction between tunnel SiO2 and ZrO2 trapping layer in SONOS type Flash memory is proposed. Cross-sectional TEM image shows that the ZrO2 is highly reactive with SiO2 to form a SixZr1-xO2 interface of graded composition over the thickness of ~2 nm. HfO2 has a similar band structure with ZrO2 but a thinner (0.5~0.7nm) interface and Si3N4 has

a smaller conduction band energy offset to SiO₂. We observed effectively enhanced programming efficiency at various operation temperatures for the devices using a charge trap layer of ZrO₂, compared to those using Si₃N₄ by ~3.2 times and HfO₂ by ~2.2 times. Furthermore, ZrO₂ demonstrates clear advantages in low-voltage operation and large V_{th} window over Si₃N₄ and HfO₂, being a very attractive material contender for next-generation NOR Flash application.

¹B. Govoreanu, et. al., IEDM Tech. Dig., p479, 2006.

²W. Cai, et. al., Physical Review B, p8573, 1986.

³R. Passler, Solid-State Electronics, p155, 1984.

⁴S. Tam, et. al., IEEE Trans. Electron Devices, vol.31, n.9, p1116, 1984.

4:00pm **NS2+EM-WeA8 Nano-Structured Surface Fabrication for Higher Luminescent LED by Self-Assembled Block Copolymer Lithography**, A. Fujimoto, K.A. Asakawa, Toshiba Corporation, Japan
INVITED

Light-Emitting Diodes (LEDs) are widely used for cell phones, display panels, LCD backlights, traffic signals, and automobile rear lamp. They are expected to be used for automobile head lamps, and interior illumination. Higher luminance LEDs are required for these purposes. The total efficiency of LEDs is determined by the product of the internal quantum efficiency and the extraction efficiency. The internal quantum efficiency has been improved more than 80 %. But, the extraction efficiency remains 10 %, because of the large difference of the refractive index between substrates ($n=3-3.5$) and the air. Therefore, to improve the extraction efficiency is the key for higher luminance LEDs. In order to improve the extraction efficiency, we fabricated nanostructures having the antireflection and the diffraction effect onto the semiconductor surface. Nanostructures have the cone, cylinder, and the mesa part. Since nanostructures have the cone and the mesa part and the refractive index from the semiconductor to the air changes smoothly within the critical angle, the incident light within the critical angle can be extracted without a loss, and the transmittance increases about 30 % compared with that of the flat surface. Furthermore, since nanostructures have the cylinder and the cylinder has the diffraction effect, the incident light over the critical angle can be extracted as the -1st order light. Nanostructures having two functions can be expected to improve the light-extraction efficiency greatly. Such structures are usually fabricated by electron beam (EB) lithography, but are too costly for mass production. To overcome this challenge, block copolymer lithography was employed. The polystyrene (PS) - polymethyl methacrylate (PMMA) diblock copolymer was used in this study. The PMMA was removed by reactive ion etching (RIE) since the PMMA has a much faster etch rate than the PS by RIE. The gallium phosphide (GaP) substrate was dry-etched by chlorine-based inductively coupled plasma RIE using the remaining PS dots as a mask. The optical extraction efficiency of the substrates with subwavelength columnar structures improved 2.6 times compared to unprocessed flat substrates; the pillars' height was 350 nm, diameter was 130 nm, and pitch was 180 nm. We also manufactured a real LED and increased light emission volume 1.8 times compared with conventional LED at the same energy consumption.

4:40pm **NS2+EM-WeA10 Current-Voltage Characteristic of Organic Molecular Wires by Conducting Atomic Force Microscopy**, N.J. Lee, S.B. Kim, I.C. Hong, S.H. Koo, Y.J. Choi, J.W. Kim, Y.S. Kim, C.J. Kang, Myongji University, Korea

Using an atomic force microscope (AFM), with conducting cantilever the current versus voltage (I-V) characteristics of difference group substituted carotenedithiol molecules are measured. The molecules are inserted into 1-methylsulfanyl-octadecane monolayer on gold surface, and a Au nanoparticle is attached to each molecule via the protruding thiol group. To measure the current a gold coated AFM probe is used to contact with the molecule through the Au nanoparticle. A self-assembled monolayer of 1-methylsulfanyl-octadecane was analyzed by the surface plasmon resonance, ellipsometry and X-ray diffraction, which were employed to identify suitable preparation conditions of the substrate. The I-V curves of two kinds of carotenedithiol molecules substituted for different end groups appear quite different because of the different electron transport properties, bromophenyl substituted group put a crimp in electron transport. The phenyl-substituted carotenoid is significantly more conductive than the bromophenyl-substituted carotenoid. In this talk, we'll present the molecular wires possibility. The carotenoid candidate "molecular wire".

5:00pm **NS2+EM-WeA11 Fabrication, Dynamics, and Electrical Properties of Shielded Probes**, P.D. Rack, B.J. Rodriguez, K. Seal, S. Jesse, A.P. Baddorf, S.V. Kalinin, Oak Ridge National Laboratory

Many biological systems respond to stimuli such as electrical bias. The application of naturally occurring local biases in biosystems can be mimicked with an atomic force microscope tip. In order to minimize capillary forces and obtain high resolution images of biosystems, a liquid environment, typically with a high ionic strength, is required. A bias applied

via traditional cantilevers will cause electrochemical reactions in the solution. The use of shielded probes may allow biases to be applied locally, and minimize any electrostatic force contribution to the signal being measured, whether the tip is used as an electromechanical probe or a probe of local electric force. In this case, the bias is applied locally and the signal is measured locally, both on the nanoscale. The fabrication of suitable shielded probes requires (a) good dynamic properties of the lever, (b) good insulation everywhere except for the apex, (c) high apex conductivity, and (d) apex geometry consistent with high resolution. In this presentation, we describe a process for fabricating shielded probes, and measure their dynamic and electrical properties. The commercial doped-Si tips were coated with an oxide prior to etching a small via (~ 200nm diameter) with a focused ion beam. Subsequent to the via etch, a tungsten contact was deposited in the via using electron beam induced deposition. The dynamic properties of the fabricated probes, as well as their performance in Piezoresponse force microscopy in ambient and liquid environment and I-V characteristics are discussed. The choice of other coatings or other metal plugs may allow for further improvements, and/or tunable properties. The use of shielded probes may allow precise control over the application and measurement of local fields in solution.

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