

Monday Afternoon, November 9, 2009

Nanometer-scale Science and Technology

Room: L - Session NS+BI-MoA

Nanowires and Nanoparticles II

Moderator: L. Bartels, University of California at Riverside

2:00pm **NS+BI-MoA1 Shape Control and Assembly of Colloidal Metal Nanocrystals**, *P. Yang*, University of California - Berkeley, *Henzie*, University of California, Berkeley **INVITED**

Colloidal metal nanoparticles are emerging as key materials for catalysis, plasmonics, sensing, and spectroscopy. Within these applications, control of nanoparticle shape lends increasing functionality and selectivity. Shape-controlled nanocrystals possess well-defined surfaces and morphologies because their nucleation and growth are controlled at the atomic level. An overall picture of shaped metal nanoparticles will be presented, with a particular focus on solution-based syntheses and assembly for the noble metals. General strategies for synthetic control will be discussed, emphasizing key factors that result in anisotropic, nonspherical growth such as crystallographically selective adsorbates and seeding processes. The application of such nanoparticles and their arrays in SERS will be discussed.

2:40pm **NS+BI-MoA3 Properties of InP/InAs/InP Core-Shell Nanopillars Grown by Metalorganic Vapor-Phase Epitaxy**, *V. Eyoen*, *L. Gao*, *S. Chowdhury*, *R. Woo*, *B. Liang*, *M. Pozuelo*, *S. Prihodko*, *M. Jackson*, University of California, Los Angeles, *N. Goel*, *M. Hudait*, Intel Corporation, *D. Huffaker*, *M. Goorsky*, *S. Kodambaka*, *R. Hicks*, University of California, Los Angeles

Compound semiconductor nanowire devices are of great interest due to their size-dependent electrical and optical properties and their potential applications in nano-electronics. In this study, we demonstrate the growth of InP/InAs/InP core-shell nanopillars by metalorganic vapor-phase epitaxy (MOVPE). Indium droplets were used to catalyze crystal nucleation at low temperature. At 400°C and a V/III ratio of 86, hexagonal pillars were grown with smooth side walls and average widths and heights of 45 and 70 nm, respectively. Scanning and transmission electron microscopy, electron backscattered diffraction, and selected area electron diffraction revealed that the pillars were single crystal wurtzite and were bounded by {1,-1,0,0} sidewalls. Indium arsenide quantum wells were deposited on the nanopillars at 395°C and a V/III ratio of 120, and then capped with a thin layer of InP. The thickness of the quantum well was ~5 nm. Photoluminescence spectra at 77 K yielded a single intense band at 1750 nm (0.7 eV) with a full width at half maximum of 350 nm. These results indicated that there was phosphorus and arsenic intermixing with formation of an InAs_xP_{1-x} alloy. Further growth experiments varying temperature, V/III ratio, and hydrogen interrupt time succeeded in shifting the photoluminescence peak closer to the band gap for InAs. Detailed measurements of the optical and electrical properties of the core-shell nanopillars will be presented at the conference.

3:00pm **NS+BI-MoA4 Synthesis of Vertically Aligned and Patterned Silicon-Carbon Core Shell Nanotubes**, *J. Song*, *R. Vanfleet*, *R.C. Davis*, Brigham Young University

Here we report the first synthesis of silicon-carbon core-shell nanotubes (SiCNTs). The SiCNTs are formed by coating a vertically aligned and patterned carbon nanotube (CNT) forest with low pressure chemical vapor deposition (LPCVD) of silicon. The carbon nanotube forests were grown from a patterned thin film Fe catalyst resulting in high aspect ratio three dimensional microscale structures up to 500 microns tall with vertical sidewalls. The density of the nanotubes in the forests is very low; the nanotubes fill only about 1 percent of the space by volume. Silicon LPCVD layers (~30 nm thickness) are deposited conformally, coating the nanotubes and significantly increasing the mechanical strength of the structure. By adjusting the silicon deposition temperature, amorphous or crystalline silicon shells can be formed. This combination of silicon LPCVD on VACNTs yields a unique fabrication approach resulting in porous three dimensional silicon structures with precise control over shape and porosity.

3:40pm **NS+BI-MoA6 Structure and Electron Transport through Molecules Assembled in Multi-Component Molecular Gradient Layers**, *N. Ballav*, *P. Morf*, Paul Scherrer Institute, Switzerland, *F. Nolting*, Swiss Light Source, Switzerland, *F. Wrochem*, *H.-G. Nothofer*, *A. Yasuda*, *J. Wessels*, Sony Deutschland GmbH, Germany, *T.A. Jung*, Paul Scherrer Institute, Switzerland

Surface molecular gradients are essential for the fast screening of molecular and cellular adhesion and motion in assays and have been used to relate

molecular binding with the biological response for functional biomolecular entities. They are being used for optimizing the properties of bio-interfaces, bio-chips, bio-assays, and bio sensors, and for controlling wettability to induce movement in water droplets. Herein we present a new method to fabricate self-assembled monolayer (SAM) based multi-component molecular gradients comprising constituents with specific head or tail groups attached to different molecular backbones. We demonstrate for the first time how local (STM) and non-local (NEXAFS) methods can be combined with theoretical calculations (DFT) to draw conclusions on structure, orientation and local processes, in particular electronic conductance in the gradient layer (1). Our achievement goes beyond previous works in the ability to visualize molecular gradient layers and to study the anisotropy of physicochemical properties with laterally changing composition.

4:00pm **NS+BI-MoA7 Reduction, Morphology, and Conductivity of Pd Nanoparticles on Pyridine-Terminated Self-Assembled Monolayers**, *C. Silién*, University of Limerick, Ireland, *M. Buck*, *S. Francis*, *M. Caffio*, *B. Wang*, *R. Schaub*, University of St Andrews, UK, *D. Lahaye*, *N.R. Champness*, University of Nottingham, UK

Metallization of organic self-assembled monolayers (SAMs) is generally impeded by the penetration of metal through the film. A two-step scheme, involving coordination of metal ions and electrochemical reduction in separate solutions [1], was recently proposed to circumvent the problem, opening up new opportunities for the preparation of low-dimensional metal structures on SAMs. This strategy was further investigated using SAMs of newly designed pyridine-terminated molecules (*o*-(4-pyridine-4-yl-phenyl)-alkanethiol, PyPn, with *n*=2,3) [2], which combine the high structural integrity and quality of biphenyl-based SAMs [3,4] with the chemical functionality afforded by the pyridine moiety. Pd adlayers on PyPn SAMs on Au(111) were prepared by reduction of Pd²⁺ either directly from solution or following the two-step scheme [1]. Scanning tunneling microscopy (STM) revealed that, in both cases, and independently of the alkane spacer length, Pd systematically organizes into nanoparticles that are weakly bonded onto the pyridine moieties (*i.e.*, easily displaced with tunnel current of the order of a few pA), exhibit a narrow height distribution around 2.4 nm and display a Coulomb gap of ~±0.20 V. These data strongly suggest that the Pd nanoparticles are not contacted with the Au substrate. Moreover, the nanoparticle coverage can be increased up to a monolayer, revealing that it is more favorable to generate new nanoparticles than to add material to existing ones. It is proposed that Pd²⁺ reduction is not mediated by structural defects in the SAM. Lateral diffusion of Pd adatoms and nanoparticles occurs on the SAM and explains the morphology of the Pd adlayer.

[1] Baunach, T.; Ivanova, V.; Kolb, D. M.; Boyen, H.-G.; Ziemann, H.-G.; Büttner, M.; Oelhafen, P. *Adv. Mater.* **2004**, *16*, 2024-2028.

[2] Silién, C.; Buck, M.; Goretzki, G.; Lahaye, D.; Champness, N. R.; Weidner, T.; Zharnikov, M. *Langmuir* **2009**, *25*, 959-967.

[3] Cyganik, P.; Buck, M.; Wilton-Ely, J. D. E. T.; Wöll, C. *J. Phys. Chem. B* **2005**, *109*, 10902-10908.

[4] Cyganik, P.; Buck, M.; Strunskus, T.; Shaporenko, A.; Witte, G.; Zharnikov, M.; Wöll, C. *J. Phys. Chem. C* **2007**, *111*, 16909-16919.

4:20pm **NS+BI-MoA8 Estimation of Thermal Conductivity of Si and Oxide-Covered-Si Nanowires by Molecular Dynamics Simulation**, *T. Saegusa*, *K. Eriguchi*, *K. Ono*, Kyoto University, Japan, *H. Ohta*, University of California, Santa Barbara

Nanowires (NWs) have attracted much attention because they are expected to be applicable to various devices such as the field-effect transistors, solar cells, and thermoelectric devices. The reason is that in nanostructures, we can see some peculiar phenomena which are not observed in bulk materials. One of the phenomena is the lower thermal conductivity of NWs [1]. The thermal conductivity of NWs is one to two orders of magnitude lower than the bulk value (~168 W/mK at 300K). This is appreciated to occur by confinement of the phonon propagation. The phonons are prevented by surface scattering due to the small wire radius. This means that surface atoms may have a great influence on material properties. Experimental observations of the thermal conductivity by P. Yang's group [1] as well as theoretical studies by different approaches such as Boltzmann transport equation, Monte Carlo (MC) method for phonon propagation [2], and molecular dynamics (MD) simulations [3] have been published. In addition, Hochbaum *et al.* experimentally observed the reduction of thermal conductivities in Si-NWs fabricated by electroless etching, where silicon NWs were coated by native oxides [4]. These studies indicate thermal conductivities are very sensitive to surface structures.

In this paper, we present the thermal conductivity of naked Si-NWs and oxide-coated Si-NWs at 300 K, evaluated by employing direct

nonequilibrium MD simulation with the Stillinger-Weber interatomic potential model for Si/O systems. The thermal conductivity was obtained for various cross sections (2-8 nm²) and lattice orientations (<100>, <111>, and <110>). The thermal conductivity for naked Si-NWs with cross sections of 2-8 nm² at 300 K was 2-10 W/mK, which was in good agreement with that for <100>-Si-NWs (1-2 W/mK) obtained from equilibrium MD simulation by Volz *et al.* [3] and from MC simulation by Chen *et al.* [2]. We found the small dependency of thermal conductivity on the lattice orientation. In case of oxide-coated Si-NWs, the thermal conductivity was reduced as the thickness of Si-oxides increased. To check our simulation results, we also analyzed the strain in Si-NW due to surface oxidized layers. Detailed simulation results and analytical approach for various surface structures or cross-sections will be shown at the conference.

- [1] D. Li *et al.*, *Appl. Phys. Lett.* **83**, 2934(2003)
- [2] Y. Chen *et al.*, *Journal of Heat Transfer, Transaction of ASME*, **127**, 1129(2005)
- [3] S.G.Volz *et al.*, *Appl. Phys. Lett.* **75**, 2056(1999)
- [4] A.I.Hochbaum *et al.*, *Nature*, **451**, 163(2008)

4:40pm NS+BI-MoA9 Temperature Dependence of Carbon Nanofiber Resistance, H. Yabutani, T. Yamada, T. Saito, C. Yang, Santa Clara University

To assess their potential for interconnect applications, the interplay between electrical and thermal transport in carbon nanofibers (CNFs) under high-current stress is examined. Current-voltage measurement results obtained during each stress cycle reveal temperature-dependent behavior of CNF resistance, the analysis of which is the subject of this paper.

To minimize the contact resistance between gold electrode and CNF, tungsten is deposited on each electrode using focused ion beam [1]. For each test device, we apply stressing current progressively, *i.e.*, in the first cycle, a small current is applied for three minutes, and in the second cycle, a slightly larger current is applied for another three minutes, etc. Using this scheme, we obtained a decrease in average resistance with increasing stressing current for each stress cycle. In ref. [2], we presented a heat transport model that takes into account Joule heat generation, dissipation, and diffusion during current stressing. In this model, the CNF temperature along its length was determined as a function of stressing current. Since the increase in temperature originates from Joule heating, and since we established that current stressing has little effect on the total resistance at ambient temperature prior to breakdown [1], this result suggests that the reversible resistance change due to Joule heating is a result of change in bulk CNF properties at elevated temperatures.

The mechanism for CNF bulk resistance decrease with temperature was discussed in the context of transport in disordered media [3]. Our CNF devices have impurities and/or lattice defects, which often serve to trap carriers. Thermal energy releases these carriers from the trap centers, giving rise to lower resistance. Thus transport is controlled by thermal activation of these trapped carriers and their subsequent re-trapping as the temperature is lowered. The same mechanism would account for the observed decrease in resistance as the temperature increases with increasing stressing current due to Joule heating.

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- [2] T. Yamada, T. Saito, D. Fabris, and C. Y. Yang, *IEEE Electron Device Lett.* **30**, 469-471 (2009).
- [3] Q. Ngo, T. Yamada, M. Suzuki, Y. Ominami, A. M. Cassell, J. Li, M. Meyyappan, and C.Y. Yang, *IEEE Transactions on Nanotechnology* **6**, 688-695 (2007).

5:00pm NS+BI-MoA10 Relative Stability of Aromatic Self-Assembled Monolayers Formed by Thiols and Selenols, K. Szelagowska-Kunstman, P. Cyganik, Jagiellonian University, Poland, B. Schüpbach, A. Terfort, Goethe-Universität Frankfurt, Germany

Aromatic self-assembled monolayers (SAMs) are considered a model system for molecular electronics applications.¹ However, potential use of these monolayers in real devices is limited by significant concentration of structural defects,² which disturb functions of the metal-molecule-metal junction. One of strategies we propose to optimize structure of aromatic SAM's is selection of proper headgroup atom binding SAMs to the substrate.^{3,4}

In this presentation we report on stability of two analogous aromatic SAMs bound to the Au(111) substrate by S or Se atom. To compare stability of both systems we analyze exchange of molecules constituting complete SAM monolayer during incubation in solution containing other aliphatic thiol or aliphatic selenol molecules.⁵ The exchange experiments have been performed by comparing not just a single SAM but two entire homologue series of BPnS (CH₃-(C₆H₄)₂-(CH₂)_n-S-, n = 2-6) and BPnSe (CH₃-(C₆H₄)₂-

(CH₂)_n-Se-, n =2-6) molecules on Au(111) surface. Quantitative control of the exchange process was obtained using Infrared Reflection Adsorption Spectroscopy. These data will be discussed together with our recent microscopic study which found that binding by selenium atoms improve significantly the ordering of these SAMs and influences molecule-substrate interaction.⁴ Obtained results clearly indicate higher stability of SAMs based on selenols in comparison to their thiol analogs.

References

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- [5] K. Szelagowska-Kunstman, P. Cyganik, B Schüpbach, A. Terfort **2009** *in preparation*

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