

Tuesday Afternoon, November 11, 2014

Nanometer-scale Science and Technology

Room: 304 - Session NS+AS+SS-TuA

Nanowires and Nanotubes: Advances in Growth and Characterization

Moderator: Lincoln Lauhon, Northwestern University

2:20pm NS+AS+SS-TuA1 **Surface Chemical Choreography of Nanowire Synthesis**, Michael Filler, S.V. Sivaram, N. Shin, I.R. Musin, Georgia Institute of Technology **INVITED**

This talk will provide an overview of our recent efforts to understand the chemical phenomena underlying semiconductor nanowire growth. The vapor-liquid-solid technique – where a liquid “catalyst” droplet collects atoms from the vapor and directs crystallization of individual solid layers – is a ubiquitous method for the synthesis of these quintessential nanoscale building blocks, but a lack of atomic-level design rules prevents robust programming of structure. Long-standing challenges in the control of heterostructure, dopant profile, atomic stacking sequence, kinking, and even simple axial growth restrict the accessible property space and highlight the pitfalls of an overreliance on empirical process optimization. We couple in-situ or operando infrared spectroscopy with post-growth high-resolution electron microscopy to connect specific surface chemical bonds present during synthesis with nanowire structure. Studies of Si and Ge nanowires demonstrate the fundamental, and previously unrecognized, role of adsorbed hydrogen atoms. The surface coverage of these precursor (e.g., Si₂H₆ or Ge₂H₆) decomposition intermediates, which we quantitatively determine as a function of pressure and temperature, can change over a narrow range and strongly influence growth. Our findings show, for example, that adsorbed hydrogen is essential for stabilizing the catalyst or driving elongation in new crystal directions for Ge and Si nanowires, respectively. We leverage these insights to rationally design precursors that choreograph nanowire structure on multiple length scales, permitting the fabrication of user-defined defect, kinking, and diameter-modulated superstructures.

3:00pm NS+AS+SS-TuA3 **Atom Probe Tomography Analysis of GaAs-AlGaAs Core-Shell Nanowire Heterostructures**, Nari Jeon, Northwestern University, S. Morkötter, G. Koblmüller, Technische Universität München, Germany, L.J. Lauhon, Northwestern University

GaAs-AlGaAs planar heterostructures have various electronic and optoelectronic applications such as solar cells and light-emitting diodes.^{1,2} This is due to a small lattice mismatch between GaAs and AlAs providing wider opportunities in bandgap tuning. Moreover, modulation doping scheme is well-known to be effective in enhancing electron mobility in the heterostructures by minimizing electron scattering from ionized impurities. Since growth of GaAs-AlGaAs core-shell nanowires was demonstrated in 2005,³ there has been a growing number of papers reporting novel (opto)electronic transport properties, which are originated from the nonparallel geometry of GaAs-AlGaAs interfaces and its related compositional fluctuations.⁴ In fact, compositional structures are more complex in the core-shell nanowires compared to the planar counterparts. For example, there are six Al-rich bands along the corners of {110} sidewall facets in the AlGaAs shell.⁵ While most of the previous studies were based on transmission electron microscopy on cross-sectioned samples, we exploited the atom probe tomography (APT) to explore compositional fluctuations in three dimensions. The focus of the presentation will be APT sample preparation and composition characterization of Si delta-doped GaAs-AlGaAs core-shell nanowires. Molecular beam epitaxy reactor was used to grow the core-shell nanowires and the GaAs-AlGaAs superlattice planar samples as a reference to the nanowires. Individual nanowires were mounted on tungsten tips using micromanipulator for APT and planar samples were fabricated into tip-shaped APT samples by the lift-out and sharpening method using focused ion beam (FIB). Carefully designed structures of the superlattice with varied thickness and spacing in planar samples enabled us to estimate the range of possible ion beam damage from FIB. The atom probe conditions such as laser pulse energy and target detection rate were also optimized to achieve high spectral and spatial resolutions, which are critical for APT of III-V compound semiconductors where preferential detection loss and surface diffusion for III and/or V group elements are possible depending on the APT conditions. Intermixing at GaAs-AlGaAs interface and stoichiometric fluctuation in AlGaAs shell were mainly studied along with the detection limit of Si dopants in the delta doping layer.

1 K. Takahashi et al. *Solar Energy Materials and Solar Cells* **66** 517-524 (2001).

2 D. Ban et al. *Journal of Applied Physics* **96** 5243-5248 (2004).

3 J. Noborisaka et al. *Applied Physics Letters* **87** 093109-3 (2005).

4 S. Funk et al. *Nano Letters* **13** 6189-6196 (2013).

5 M. Heiss et al. *Nature Materials* **12** 439-444 (2013).

3:20pm NS+AS+SS-TuA4 **Scanning Tunneling Microscopy of Semiconductor Nanowire Surfaces and Devices**, R. Timm, J. Knutsson, M. Hjort, S. McKibbin, O. Persson, J.L. Webb, Anders Mikkelsen, Lund University, Sweden

III-V semiconductor nanowires (NWs) offer tremendous possibilities for device application in solid-state lightning, energy conversion, and information technology [1]. With their small diameter and their very large surface-to-volume ratio, the NW device behavior is strongly determined by their surface structure. Thus, it is both essential and challenging to investigate their atomic surface structure and to combine this information with electrical measurements on individual NWs.

Recently, we have managed to clean InAs NWs from their native oxide and revealed the atomic arrangement of their side surfaces with scanning tunneling microscopy (STM). Here, we present STM images of various NW surfaces of both wurtzite and zincblende crystal structure [2], including InAs, GaAs, InP, and InSb NWs. By combining STM imaging with scanning tunneling spectroscopy (STS) measurements, we simultaneously study the surface structure and local electronic properties across the interfaces of NW heterostructures [3].

For correlating local structural and electronic characterization with transport measurements of NW devices, we have developed a novel STM-based setup: We are using combined atomic force microscopy (AFM) and STM/S on individually contacted NWs for mapping the surface structure and the local band alignment along the NW heterostructure under device performance. We show initial results of this unique approach on InAs-GaSb nanowire tunnel diodes, where we could prove Esaki behavior of a NW while it was investigated by STM/AFM. From a set of STS spectra we determined the position of the Fermi level along the nanowire for different applied biases, showing an abrupt drop directly at the material interface. In a reverse experiment, we used the STM/AFM tip as local gate and measured the resulting source-drain current through the nanowire for different biases [4].

In some cases it is desirable to measure the conductivity of individual as-grown nanowires in an upright-standing configuration without any sample processing. Here we have developed an alternative setup where the STM tip is used to first image free-standing nanowires from top and then form a point contact [5]. We will demonstrate the reproducibility of this method in establishing low-resistive Ohmic contacts to individual InP and InAs nanowires [6], and we will show initial results on the I-V properties of individual InP NW solar cells.

[1] J. Wallentin *et al.*, *Science* **339**, 1057 (2013)

[2] M. Hjort *et al.*, *Nano Lett.* **13**, 4492 (2013)

[3] M. Hjort *et al.*, *ACS Nano* **6**, 9679 (2012)

[4] J. L. Webb *et al.*, *Nano Res.*, in print

[5] D. B. Suyatin *et al.*, *Nature Commun.* **5**, 3221 (2013)

[6] R. Timm *et al.*, *Nano Lett.* **13**, 5182 (2013)

4:20pm NS+AS+SS-TuA7 **Poly-Aromatic Hydrocarbon Nanostructure Growth on Single and Multi-Layer Graphene**, Alexander Yulaev, CNST/UMD Graduate Student Researcher, A. Kolmakov, NIST

Poly-aromatic hydrocarbons (PAH) are known as potential hazardous organic pollutants, which can be found in soil, air, meat, fish and etc. Carbon based materials are routinely used for environmental remediation. Graphene has ultrahigh surface area and can be seen therefore as an “ultimate carbon filter”. In our communication we report PAH nanostructure nucleation and growth on a single and multi-layer graphene CVD grown on a copper substrate. The PAH deposition was performed by thermal evaporation in vacuum, and resultant morphology of a PAH was studied by means of SEM as a function of time, rate, substrate temperature and graphene thickness. We found that PAH predominantly grows in a form of nanowires which have a good vertical alignment with respect to a graphene plane. It was shown that temperature of a substrate, deposition rate of PAH, and number of graphene layers were the key parameters to control the PAH morphology such as a nucleation density and diameter of PAH nanowires. We relate the orthogonal growth of PAH nanowires to the discotic nature of PAH molecules forming weak VDW interactions with a graphene basal plane and lamella like structures due to favorable face-to-

face intermolecular interaction. We envision PAH nanostructures grown on a graphene substrates may help optimize PAH filters.

4:40pm **NS+AS+SS-TuA8 Using Surface Chemistry to Direct the *In Situ* Synthesis and Placement of Nanowires**, A.A. Ellsworth, J. Yang, Z. Shi, Amy Walker, University of Texas at Dallas

Nanoscale one-dimensional materials, commonly called nanowires, have properties that differ significantly from their bulk counterpart materials, and thus have applications in areas including sensing, energy conversion, electronics and optoelectronics. One of the major challenges in the practical use of nanowires is their integration into complex functional structures in a predictable and controlled way. We have recently introduced two promising new techniques by which to direct the growth of metallic and semiconducting nanowires. ENDOM, or Electroless Nanowire Deposition On Micropatterned substrates, employs electroless deposition (ELD) to form metallic nanowires on substrates. SENDOM, or Semiconductor Nanowire Deposition on Micropatterned surfaces, uses chemical bath deposition (CBD) to deposit semiconductor nanowires. SENDOM and ENDOM are generally applicable to the preparation of metallic, semiconducting, and even insulating nanostructures on many technologically relevant substrates. These techniques have several advantages over existing *in situ* synthesis and placement methods: it is fast, and it does not require expensive lithographic equipment or a clean room.

Using ENDOM or SENDOM we are able to create nanowires that are ultralong (centimeters) and follow complex paths such as a right-angle or a curve. We illustrate ENDOM by deposition of Ni, Cu, Pd and other nanowires on patterned -OH/-CH₃ SAMs. We exploit the different deposition rates electroless deposition of metals using dimethylamine borane (DMAB) on -CH₃ and -OH terminated SAMs to deposit nanowires. We illustrate SENDOM by deposition of CuS nanowires on patterned -COOH/-CH₃ SAMs. In this case, the deposition is controlled by the interaction of thiourea (sulfur source) with the SAM surface. In this paper we discuss the reaction pathways involved in the formation of these nanowires including the nucleation sites and the dependence of the nanowire growth on pH and deposition temperature.

5:20pm **NS+AS+SS-TuA10 Development of New Nanocatalysts through Restructuring of Co₃O₄ Nanorods Anchored with Pt Atoms**, Shiran Zhang, University of Notre Dame, A. Frenkel, Brookhaven National Laboratory, F. Tao, University of Notre Dame

Low-temperature water-gas shift (WGS) reaction is crucial for low-temperature fuel cell technology as it provides a solution for on-board hydrogen purification near operational temperature. Design of catalysts with lower activation energy and higher activity is critical for a practical application. Significant effort has been devoted to development of new WGS catalysts with high activity at low temperatures. Most of them are metal nanoparticles supported on reducible oxides such as CeO₂ or TiO₂.

Here we reported two nanocatalysts, PtCo_n/Co₃O₄ and Pt_mCo_m/CoO_{1-x} that are highly active for low-temperature WGS reaction. They were prepared by restructuring singly dispersed Pt atoms supported on Co₃O₄ nanorods through a controlled reduction. The single dispersion of Pt atoms on cobalt oxide nanorods was confirmed with high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM). Photoemission features of Co2p and Pt 4d_{5/2} of these catalysts during catalysis were tracked with ambient pressure x-ray photoelectron spectroscopy (AP-XPS) using monochromated Al K α . Coordination environment of Pt atoms was tracked with in-situ extended x-ray absorption fine structure spectroscopy (EXAFS). These ex-situ and in-situ studies show that two new active phases, PtCo_n/Co₃O₄ and Pt_mCo_m/CoO_{1-x} were formed in the temperature ranges of 150 °C – 200 °C and 280 °C – 350 °C in the mixture of 3 Torr CO, 1 Torr H₂O, respectively. The formation of singly dispersed bimetallic sites PtCo_n anchored on Co₃O₄ was confirmed with in-situ EXAFS studies. The formed Pt_mCo_m nanoclusters supported on CoO_{1-x} in the temperature range of 280 °C – 350 °C was identified with HAADF-STEM. Kinetics studies in the gas mixture of carbon monoxide and water vapor with a ratio of 3:1 revealed that activation barriers for PtCo_n/Co₃O₄ at 150-200 °C and Pt_mCo_m/CoO_{1-x} at 150-250 °C are 50.1±5.0 kJ/mol and 29.6±4.0 kJ/mol, respectively. Turn-over frequencies (TOFs) of the two new catalysts PtCo_n/Co₃O₄ and Pt_mCo_m/CoO_{1-x} at 150 °C are larger than those of Pt and Au nanoparticles supported on CeO₂ and TiO₂ catalysts by one magnitude. The excellent activities of the new catalytic phases PtCo_n/Co₃O₄ and Pt_mCo_m/CoO_{1-x} formed through restructuring the singly dispersed Pt atoms on Co₃O₄ suggest a method of developing new catalysts through restructuring singly dispersed catalyst atoms such as noble metals on an oxide support.

5:40pm **NS+AS+SS-TuA11 A Study of Single-Walled Carbon Nanotubes Coated with Iron Oxide (Fe₂O₃) Nanoparticles for Enhanced Magnetic Properties**, Suman Neupane, D. Seifu, Morgan State University
Carbon nanotubes (CNTs) continue to attract significant interest due to their extraordinary thermal, electrical, optical, and mechanical properties. The preparation of CNTs coated with magnetically sensitive Fe₂O₃ nanoparticles has implications to the development of advanced heat transfer nanofluids and high capacity lithium ion batteries. In this report, single-walled carbon nanotubes (SWNTs) were uniformly coated with Fe₂O₃ nanoparticles through solution mixture. Scanning and transmission electron microscopy were used to compare the surface morphology of pristine SWNTs and as-prepared SWNTs coated with Fe₂O₃ nanoparticles. Raman spectroscopy and thermo gravimetric analysis presented the extent of defects and the amount of Fe₂O₃ nanoparticles present in the sample. Near edge X-ray absorption fine structure spectroscopy was used to probe the electronic band structure of as-prepared core-shell structures. Magnetization measurements indicate that the coercive field of SWNTs coated with Fe₂O₃ nanoparticles was twice that of pristine SWNTs.

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