

# Tuesday Morning, November 1, 2011

Nanometer-scale Science and Technology Division  
Room: 203 - Session NS-TuM

## Nanowires and Nanoparticles II: Characterization and Synthesis

Moderator: U.D. Schwarz, Yale University

8:00am **NS-TuM1 Formation of Metallic Glass Nanofiber**, *K.S. Nakayama, Y. Yokoyama, T. Wada, N. Chen*, Tohoku University, Japan

Metallic glasses have been receiving significant attention because their superior mechanical properties are attractive to structural materials. However, far less attention paid to metallic glass nanostructures though they have exciting potential for catalysis applications due to the expanding of metallic surface area. Progress has been hindered by the lack of bottom-up methodologies to produce self-assembly nanostructures. Recently, we show that the instantaneous fracture process of a bulk metallic glass produces amorphous nanostructures [Nakayama et al., Nano Lett. **8**, 516 (2008)] and the simple tensile draw under viscous deformation leads to the formation of individual amorphous nanowires [Nakayama et al., Adv. Mater. **22**, 872 (2010)]. However, these approaches are unsuitable for massive production because the amount of nanowires is limited. In this talk, we first report an approach to the synthesis of metallic glass nanofibers that exploits a conventional gas atomization which is a central technique in powder metallurgy. We found that the nanofiber forming ability is closely related to the super liquid cooling region of the alloys and the atomizing gas pressure.

8:20am **NS-TuM2 Plasma-assisted Dissociation of Organometallic Vapors for Continuous, Gas-Phase Preparation of Multimetallic Nanoparticles**, *R.M. Sankaran, P. Lin*, Case Western Reserve University

Metal nanoparticles (NPs) are desired for novel optical, magnetic, electric, and catalytic applications. Recently, there has been growing interest in *multimetallic NPs*, a special class of metal NPs composed of two or more distinct metal elements with alloyed, core-shell, or other architectures. Despite the development of numerous synthetic routes for metal NP synthesis, the preparation of multimetallic NPs with controlled size, composition, morphology, and purity remains a significant challenge.

Here, we present a single-step, continuous, gas-phase process that is capable of producing a wide range of size- and compositionally-tuned multimetallic NPs [12]. Our approach is based on plasma-assisted dissociation of metal-organic vapors which is a well-established technique for chemical vapor deposition (CVD) of thin films of metals. In our case, these same precursors are dissociated in a continuous-flow, atmospheric-pressure microplasma to homogeneously nucleate metal NPs. To synthesize multimetallic NPs, more than one precursor is mixed in the microplasma reactor. The size of the multimetallic NPs is controlled by the total vapor concentration of the precursors while the atomic-scale composition is controlled by the relative ratio of the different metal precursors. Bimetallic and trimetallic NPs of various metals including Ni, Fe, Cu, and Pt, have been produced by this approach. In this talk, we will discuss our experimental method in detail, as well as the structural properties of the NPs as determined by *in situ* aerosol measurements, high-resolution transmission electron microscopy (HRTEM), energy-dispersive spectroscopy (EDS), and X-ray diffraction (XRD).

### References

1. W-H. Chiang and R.M. Sankaran, Adv. Mater. , 4857 (2008).
2. P. A. Lin and R. M. Sankaran, submitted.

8:40am **NS-TuM3 Electrical Characterization of III-V Semiconductor Freestanding Nanowires with Scanning Tunneling Microscopy**, *O. Persson, D. Suyatin, J. Wallentin, L. Samuelson, A. Mikkelsen, R. Timm*, Lund University, Sweden

Semiconductor nanowires show great characteristics for implementations in a broad range of applications, e.g. optoelectronic devices [1]. The increased possibilities of using different materials to realize tailored *p-n*-junctions or bandgaps and the inherent property of low density of defects make the nanowire the perfect candidate to realize new electronic devices.

Vast arrays of freestanding nanowires are used in many applications such as LEDs and solar cells. The electronic properties of such wires are essential to investigate for understanding and further developing the devices. The prevalent method used to make electronic measurements on nanowires is complex and challenging. It consists of several processing steps where the nanowire has to be deposited onto a substrate, localized, and then contacts need to be defined and deposited [2]. The range of nanowire material

systems and doping levels for which this method can provide good Ohmic contacts is strongly limited.

Here we show a novel technique for investigating the electronic properties of freestanding nanowires by utilizing a scanning tunneling microscope (STM). We can exactly obtain the position of individual freestanding nanowires by scanning them from the top [3]. By contacting the Au-seed particle on the top of the nanowire with the STM tip in a controlled manner, a well-defined point contact is established. The sample substrate will act as a back contact establishing a well-defined system in an ultra-high vacuum.

We have previously performed a variety of successful STM measurements on III-V nanowires [3,4]. Here we show that *I-V* measurements on single as-grown wires can be done reproducibly and consistently. GaAs wires with a doping concentration of  $10^{18}$  cm<sup>-3</sup> and a diameter of 80 nm are analyzed with this method and they consistently show a resistivity of approx. 700 Ω. Measurements on InP and InAs wires confirm the reliability of this new technique by revealing nanowire conductivities which agree well to the corresponding doping level. We will also present first results on individual nanowire *p-n*-junctions and Schottky diodes.

The main advantages of our method are that we get a well-defined contact, the measurements are done on as-grown nanowires, and we have a good control of the wire surfaces due to UHV conditions. To determine the chemical surface composition of these wires, the *I-V* studies are complemented by high intensity X-ray photoemission spectroscopy at the MAX-II synchrotron in Lund.

- [1] Li *et al.*, Mater. Today **9** (10), 18 (2006)
- [2] Suyatin *et al.*, Nanotechnology **18**, 105307 (2007)
- [3] A. Fian *et al.*, Nano Lett. **10**, 3893 (2010)
- [4] E. Hilner *et al.*, Nano Lett. **8**, 3978 (2008)

9:00am **NS-TuM4 Semiconductor Nanowires: From Materials Physics to Devices**, *L. Samuelson*, Lund University, Sweden **INVITED**

The field of self-assembled growth of semiconductor nanowires has emerged as a powerful way to form advanced materials and devices on the 10nm-scale. In this talk I will review the state of the art of the field, exemplified by our recent progress in growing ideal and defect-free III-V and III-nitride nanowires, on either III-V or silicon as substrates. I will discuss the hot materials physics aspects of structural control and the influence of zincblende vs wurtzite crystal structures on materials properties. I will then review recent progress in realizing various electronic as well as opto-electronic devices, such as nanowire field-effect transistors, tunnel devices, solar-cells as well as light-emitting diodes.

9:40am **NS-TuM6 Self-Catalyzed Growth of InP<sub>1-x</sub>Sb<sub>x</sub> Nanowires on InP(111)B**, *C. Ngo, M. Pozuelo, M. Mecklenburg, H. Zhou, B.C. Regan, R.F. Hicks, S. Kodambaka*, University of California Los Angeles

Group III-V semiconductors possess high carrier mobilities and small band gaps, making them applicable to nanoelectronics and optoelectronics.[1] Properties of these materials can in principle be controllably tuned by the fabrication of low-dimensional structures, such as nanowires. Nanowires are most commonly grown via the vapor-liquid-solid (VLS) process using Au as the catalyst. A variant of this approach is the self-catalyzed VLS process, where one of the elements of the growing material promotes the one-dimensional growth can also yield nanowires. Recent studies show that InP and InP<sub>1-x</sub>Sb<sub>x</sub> nanostructures can be grown via metalorganic chemical vapor deposition (MOCVD) using indium and indium-antimonide droplets as catalysts.[2] In this talk, we present results from studies focused on understanding the influence of metalorganic precursor flow rates on the compositional and structural evolution of InP<sub>1-x</sub>Sb<sub>x</sub> alloy nanowires.

All of our samples are grown via MOCVD using trimethylindium (TMIn), tertiarybutylphosphine (TBP), and trimethylantimonide (TMSb) as precursors, with liquid indium droplets as the catalysts and InP(111)B as substrates. The as-grown structures are characterized using scanning and transmission electron microscopies, selected area electron diffraction, energy dispersive x-ray spectroscopy, and scanning TEM to determine their morphology, crystallinity, and composition.

We demonstrate the successful growth of InP<sub>1-x</sub>Sb<sub>x</sub> alloy nanostructures of desired Sb content that is tunable with substrate temperature and TMSb flow rate. Interestingly, doubling the precursor flow rates, at a given temperature, leads to crystallization of pure wurtzite-structured InSb at the catalyst-wire interface. We attribute this phenomenon to the precipitation of excess Sb present in the indium droplets during InP<sub>1-x</sub>Sb<sub>x</sub> alloy growth. By taking advantage of the differences in growth kinetics of InP and InSb, we demonstrate the formation of compositionally-abrupt interfaces in InP/InSb axial nanowire heterostructures.

[1] M. Pozuelo, S.V. Prikhodko, R. Grantab, H. Zhou, L. Gao, S.D. Sitzman, V. Gambin, V.B. Shenoy, R.F. Hicks, and S. Kodambaka, "Zincblende to Wurtzite Transition During the Self-catalyzed Growth of InP Nanostructures" *J. Crystal Growth* **312**, 2305 (2010).

[2] H. Zhou, M. Pozuelo, R.F. Hicks, and S.Kodambaka, "Self-catalyzed vapor-liquid-solid growth of  $\text{InP}_{1-x}\text{Sb}_x$  nanostructures" *J. Crystal Growth* **319**, 25 (2011).

10:40am **NS-TuM9 The Surface Hydrogen-Controlled Crystal Structure of Group IV Nanowires**, *N. Shin, M.A. Filler*, Georgia Institute of Technology

Semiconductor nanowires offer exciting opportunities to fabricate high performance devices for energy conversion, photonics, and quantum computation. The precise control of crystal structure and geometry is required to achieve a desired behavior, especially in highly confined nanoscale systems. Unfortunately, a fundamental understanding of the surface chemistry that controls surface energetics is currently lacking, despite its critical importance for robust synthesis. Although hydrogen is prevalent during the hydride-based vapor-liquid-solid growth of semiconductor nanowires, its role is largely unknown. To this end, we systematically studied the effect of hydrogen during the growth of Si nanowires and confirmed its influence on crystal growth direction, catalyst ripening, and sidewall faceting for the first time. *In-situ* transmission infrared (IR) spectroscopy was used to identify the presence and bonding of hydrogen on Si nanowires as a function of growth conditions. Si nanowires were grown via a two-step process: (1) brief nucleation at high temperature (550°C) and low pressure ( $5 \times 10^{-5}$  Torr) followed by (2) elongation under different conditions (400 – 500°C,  $5 \times 10^{-5}$  –  $5 \times 10^{-3}$  Torr). Vertically-oriented epitaxial Si nanowires with uniform densities, diameters, and lengths were obtained with this method. *In-situ* IR data recorded in real-time reveals the evolution of surface Si-H stretching modes near 2090  $\text{cm}^{-1}$  and 2075  $\text{cm}^{-1}$ . Our data indicates that surface-bound hydrogen is responsible for changes in crystal orientation even for relatively large diameter nanowires. More specifically, the surface energy of the nuclei-vapor interface near the triple-phase-boundary is dramatically reduced by hydrogen adsorption and drives a transition from <111> to <112> oriented growth. We propose a simple nucleation model that explains this observation. This knowledge is then applied to rationally fabricate nanowire superstructures through the judicious incorporation of small quantities of Ge during growth. This work demonstrates the important role that surface chemistry plays in the growth of semiconductor nanowires, and the extensive use of hydride chemistries for most group IV and III-V semiconductor nanowire syntheses suggests significant implications for many materials systems.

11:00am **NS-TuM10 Inhomogeneous Longitudinal and Radial Dopant Distribution Measurements in Si Nanowires Using Scanning Auger**, *J.S. Hammond, D.F. Paul*, Physical Electronics, *U. Given*, Northwestern University

The incorporation of electrically active dopants into nanowires (NW) is essential to the development of semiconductor NWs based electronic devices. The ability to engineer the electrical properties of nanowires grown by the vapor liquid solid (VLS) process is currently limited by our incomplete understanding of the doping mechanism. Recently, several studies have shown evidence of inhomogeneous radial dopant distributions in Si NWs and the resulting effects on their electrical properties [1-2]. However, the longitudinal dopant profile has not been addressed to the same extent. Studies employing both indirect and direct measurement techniques (such as scanning photocurrent microscopy, Kelvin probe force microscopy and atom probe tomography) have addressed variations in longitudinal dopant profiles in Si NWs and related them to radial dopant variations induced by the growth process [3-4]. There have not yet been direct measurements of dopant concentrations along VLS grown nanowires. We have measured the longitudinal and radial doping profiles of phosphorus doped, untapered Si NWs using scanning Auger. We have found order of magnitude enhancements in the dopant concentration toward the NW's base as expected from previous indirect measurements. Importantly, the physical dopant profile is not identical to the active dopant profile, as shown by comparison with scanning photocurrent microscopy and Kelvin probe force microscopy measurements. The resolution and sensitivity of scanning Auger as an analytical tool for dopant concentration measurements will be compared to the other available techniques to indicate unique capabilities that can advance our understanding of nanowire doping.

[1] E. Tutuc, J. O. Chu, J. A. Ott, and S. Guha. *Appl. Phys. Lett.* 2006, 89, 263101

[2] P. Xie, Y. Hu, Y. Fang, J. Huang and C.M. Lieber, *Proc. Natl. Acad. Sci. USA* **2009**, 106, 15254-15258; E. Koren, N. Berkovich, and Y. Rosenwaks, *Nanoletters*, **2010**, 10, 1163-1167.

[3] J. E. Allen, D. E. Perea, E. R. Hemesath, and L. J. Lauhon. *Adv. Mater.* **2009**, 21, 3067-3072.

[4] E. Koren, Y. Rosenwaks, J. E. Allen, E. R. Hemesath, and L. J. Lauhon. *Appl. Phys. Lett.* **2009**, 95, 092105.

11:20am **NS-TuM11 Crystal Structure Engineering of Ge Nanowires**, *I.R. Musin, M.A. Filler*, Georgia Institute of Technology

Semiconductor nanowire engineering provides a promising route to achieve next generation energy conversion, photonic, and electronic materials. In order to enable the appropriate function for a particular application, control of nanowire crystal structure (e.g. lattice, orientation, faceting) is critical. Unfortunately, this remains a challenging task with bottom-up nanostructure syntheses. To this end, we rationally control Ge nanowire crystal structure for the first time via the addition of bifunctional alkylgermanes, which adjust the interface energetics near the three-phase line. More specifically, Ge nanowires are grown using the vapor-liquid-solid (VLS) technique with germane combined with methyl-, ethyl- or tertbutyl-germane. Scanning electron microscopy (SEM) and high resolution transmission electron microscopy (TEM) reveal that nanowires transition to a new growth direction upon addition of an alkylgermane, but remain single crystalline throughout. For the case of methyl-germane, nanowires transition from the <111> to <110> crystal growth direction. A significant reduction in tapering is also observed in all cases. Infrared spectroscopy (IR) shows that nanowire sidewalls are alkyl terminated and X-ray photoelectron spectroscopy (XPS) indicates this termination reduces the rate of oxidation. The impact of alkylgermane identity and surface coverage on crystal growth direction will be discussed in detail. The control of interface chemistry demonstrated by this work provides an important new handle for controlling nanowire structure and properties. Furthermore, the ability to effectively passivate nanowire sidewalls during growth is expected to enable more robust doping profiles by only permitting precursor incorporation through the catalyst tip.

11:40am **NS-TuM12 Towards an Understanding of Ligand Selectivity in Nanocluster Synthesis**, *S. Hong, G. Shafai*, University of Central Florida, *M. Bertino*, Virginia Commonwealth University, *T.S. Rahman*, University of Central Florida

Gold nanoclusters have been known to have a high catalytic reactivity. However, the difficulty in the synthesis of monodisperse nanoclusters (typically consisting of fewer than 100 atoms) in large amounts has been a considerable hurdle to catalytic research. Recently, bidentate ligands of the general formula  $\text{P(Ph)}_2\text{-(CH}_2\text{)}_M\text{-P(Ph)}_2$  {labeled LM}, where Ph = phosphine and M is the length of the aliphatic chain separating the P atoms, is found to remarkably have the size selecting capacity for gold nanoclusters depending on M. To investigate the origins of size selectivity of the diphosphine ligands towards small-sized Au clusters, we performed scalar relativistic density functional theory (DFT) calculations using the projector augmented wave scheme (PAW). We find that a diphosphine with long spacer such as L5 can relieve a strain induced by the spacer more easily than can one with short spacer such as L3. Hence, while L5 can interact effectively with a broad range of gold clusters of various sizes, L3 can interact only with a narrow range of gold clusters demonstrating its size-selecting power towards small gold clusters such as Au<sub>11+3</sub>. Based on these results, we propose a two-body ligand system for an ideal, highly-selective ligand, in which one part of the ideal ligand provides a high reactivity towards the broad range of gold clusters and the other part of the ideal ligand provides the control over the reactivity, which could be the form of a short length of spacer, as in diphosphine, but not necessarily limited to, or any type of controllable, reactivity-poisoning component. The controllable competition between the two components of an ideal, highly-selective ligand system will produce a desirable selectivity for the generation of monodisperse nanoclusters of interest through tailoring process.

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