Nanometer-scale Science and Technology
Room: 12 - Session NS+EN-TuM

One-Dimensional Nanowires and Nanotubes
Moderator: M.C. Hersam, Northwestern University

8:00am **NS+EN-TuM1 Direct Observation of Selective Band Engineering of an Isolated Subnanometer Wire**, ***I. Song***, *D.-H. Oh, C.-Y. Park, J.R. Ahn*, Sungkyunkwan University, Republic of Korea

Band engineering has been achieved mainly by substituting an atom of a pristine nanomaterial with an extra atom. At the ultimate nanometer scale, subnanometer scale, a nanowire becomes closer to an ideal 1D system and the band engineering by the atomic substitution enters a different regime. The strong disorder by the atomic substitution tends to break a pristine 1D system. In the band engineering of the subnanometer wire (hereafter subnanowire), we needs to find a way of circumventing the dilemma of doping and disorder. There is another challenging problem to find out a conclusive experimental proof that its electronic band structure is changed within a single isolated subnanowire. A unique experimental way is to measure its electronic band structure by angle-resolved photoemission spectroscopy (ARPES). Because a photon beam in ARPES measurement cannot be focused down to subnanometer scale, a single subnanowire cannot be used and rather subnanowires have to be aligned along a specific direction on a surface. A fundamental requirement to resolve the puzzling problem is that subnanowires have to be aligned by a self assembly method. In comparison to the atomic structure, its electronic structure is required to be decoupled to observe a 1D electronic structure change of a single isolated subnanowire by a dopant. In this study, self-assembled subnanowires on a stepped surface, Au-induced subnanowires on a Si(553) surface, were chosen. A Si(553) surface, which is one of stepped Si(111) surfaces, has an appropriate terrace width to assemble subnanowires along its step edge direction and its step edge structure can decouple subnanowires electronically. Three different metallic subnanowires exist on its single terrace and each metallic wire has only a single metallic band. After extra Au atoms were adsorbed on the self-assembled subnanowires at room temperature, only one of metallic bands moved rigidly to a higher binding energy without a change in other metallic bands, which was directly observed by ARPES measurement. Here we note that if the three metallic subnanowires are coupled electronically to each other, all of the three metallic bands have to shift rigidly. This experimentally proves that only one of self-assembled multiple metallic wires can be controlled electronically by a dopant and the electronic structure of an isolated wire can be controlled down to a subnanometer scale.

8:20am **NS+EN-TuM2 Growth of ZnO Nanowires on Retroreflector Microspheres and the Resulting Plasmonic Light Channeling Properties**, ***S.M. Prokes***, *O.J. Gembocki, E. Cleveland*, Naval Research Laboratory

We investigated the growth of ZnO nanowires on retroreflectors in order to potentially enhance the optical response of these composite structures. Results show that the growth of ZnO aligned NW arrays can be achieved on the retroreflectors, but it occurs far away from the Zn vapor source compared to the standard ZnO nanowire growth on a flat Si substrate. In the case of the ZnO nanowires on flat Si, the nanowires that formed in nearly aligned arrays were short and significantly thicker, suggesting that the growth occurred both longitudinally and laterally in this process. For the NW growth on the curved retroreflectors, as the distance from the vapor source increased, the NW density increased and for the substrates farthest from the source, growth of nearly aligned NW arrays was noted. Initially, the ZnO growth on the retroreflectors resulted in a high rate of deposition of a polycrystalline ZnO film and as the amount of Zn vapor decreased, the vapor-solid (VS) nucleation of random NWs began, and aligned nanowire arrays only formed where the vapor supply was the lowest. The fact that it is more difficult to nucleate and grow ZnO NW arrays on the retroreflectors is likely due to the surface roughness, as well as the crystal structure of the retroreflector bead.

Once nearly aligned arrays of ZnO nanowires on the retroreflectors were formed, we investigated their optical properties by forming ZnO/Ag composite NW structures and using a self assembled monolayer of benzenethiol to measure a surface enhanced Raman (SERS) response. The ZnO/Ag NW composites were formed by atomic layer deposition (ALD) of Ag, and the surface enhanced Raman (SERS) response was measured and compared to nanowire composites deposited on a flat Si substrate. Results indicated that the SERS response was 29 times greater in the case of the ZnO/Ag NW aligned arrays grown on the retroreflectors. Since one would only expect a factor of 4 enhancement due to the light reflecting properties of the retroreflector, it is suggested that the enhancement in the SERS signal is due to light channeling by the nearly aligned nanowire arrays as a result of plasmonic effects. These results have been modeled using COMSOL electric field simulations, which support the light channeling concept.

8:40am **NS+EN-TuM3 Optical and Electrical Characteristics of Al-doped ZnO Nanowires Grown by Chemical Vapor Deposition**, ***G. Shen***, *N. Dawahre, J. Waters, J. Krafcik, S.M. Kim, P. Kung*, University of Alabama, Tuscaloosa

Zinc oxide (ZnO) is a well-known major semiconductor material for optoelectronic devices due to its wide bandgap (~3.3 eV) and large exciton binding energy (~60 meV). One dimensional ZnO nanowires have been successfully synthesized by various techniques ranging from as simple as thermal chemical vapor deposition and solution growth, to more complex such as metal organic chemical vapor deposition, with good structural, optical and electrical properties. These are promising as an alternative to indium tin oxide as a more abundant, lower cost transparent window for a number of optoelectronic devices, including photovoltaics, while at the same time offering potentially more efficient electron charge transport. ZnO is also capable of harvesting the short wavelength spectral bands more efficiently.

In this work, we present the growth, doping and characterization of vertical well-aligned ZnO nanowire arrays. The wires are synthesized without metal catalyst by thermal chemical vapor deposition on basal plane sapphire substrates following the carbo-thermal reduction of zinc oxide powder. Control of the aluminum doping is accomplished by adjusting the ratio of Al and ZnO in the source material. The effects of doping and synthesis conditions on the nanowire optical and electrical properties are investigated through a number of techniques. The concentration of Al in the crystal is determined by energy dispersive spectroscopy, while atom probe tomography enables us to investigate the distribution of aluminum within the ZnO matrix. Micro-Raman spectroscopy and micro-photoluminescence, including their temperature dependence, are used to probe the vibrational and optical properties of the nanowires as a function of doping. It is observed that a defect related radiative green emission in ZnO is significantly reduced after Al doping. The electrical characteristics of undoped and doped nanowires are compared by leading electrical nano-connections to individual nanowires, which show a more than 1 order of magnitude decrease in the resistivity after doping down to 1 ohm.cm.

9:00am **NS+EN-TuM4 Rational Defect Engineering in Silicon Nanowires**, *N. Shin*, ***M. Filler***, Georgia Institute of Technology

Group IV nanowires synthesized via the vapor-liquid-solid (VLS) technique do not frequently exhibit planar defects and/or polytypic domains. Even in group III-V nanowires, where these structural motifs are common, rational control of their position remains challenging. Since defect energetics are similar in both systems, the observed structural differences are especially striking and indicate that the underlying physical phenomena are not sufficiently well understood. Here, we demonstrate how user-defined changes in surface chemistry near the triple-phase line can introduce twin planes and stacking faults during the growth of <111> oriented Si nanowires. More specifically, the addition of atomic hydrogen during Si nanowire growth enables {111} defects that begin at the <112> sidewall and continue to propagate across the nanowire even after the flux of atomic hydrogen ceases. Real-time *in-situ* infrared spectroscopy measurements reveal that covalent Si-H bonds are responsible for the defect initiation process and a simple mechanistic model will be presented to explain these results. Our findings are an important step toward a fundamental understanding of the chemistry that governs semiconductor nanowire synthesis and suggest a new route to engineer the properties of Si.

9:20am **NS+EN-TuM5 Ultrafast Carrier Dynamics of Si Nanowires Grown by LPCVD**, ***A. Seyhan***, Tokyo Institute of Technology and Nigde University, Turkey Japan, *T. Ishikawa, S. Koshihara, M. Simanullang, K. Usami, S. Oda*, Tokyo Institute of Technology, Japan

This paper report the ultrafast carrier dynamics in silicon nanowires (NWs) grown by vapour-liquid-solid (VLS) mechanism in the low pressure chemical vapour deposition (CVD) reactor at 425°C. The femtosecond transient absorption measurements were studied by tuning probe wavelength in visible range to investigate the effect of pump and probe beam polarization, NW diameter, and pump fluence on the carrier dynamics. The fast carrier relaxation with lifetime of several picosecond in Si NWs can be attributed to surface trap states. This study has important implications in the understanding of ultrafast carrier dynamics of Si NWs.

9:40am **NS+EN-TuM6 Selective Deposition of Germanium Nanowire Segments via a Hybrid Oxide-Stabilized/Vapor-Liquid-Solid Growth Method**, ***C.J. Hawley***, *T. McGuckin*, *J.E. Spanier*, Drexel University

The introduction low levels of oxygen during the vapor-liquid-solid growth (VLS) of germanium nanowires causes an oxide sheath to form at the catalyst/nanowire/vapor interface for the extent that the growth persists. This results in extremely high aspect ratio nanowires due to the removal of homoepitaxial deposition and the finite energy required for heterogeneous nucleation of germanium on its oxide. Furthermore, with the removal of oxygen, the catalyzed oxide sheath terminates and conventional growth with finite sidewall deposition dominates subsequent growth. The successful transition between the aforementioned oxide-stabilized and conventional VLS regimes can be deliberately manipulated to grow finite conical nanowires segments with discontinuous changes in diameter.

Work was supported by the U.S. Army Research Office (W911NF-08-1-0067).

10:40am **NS+EN-TuM9 Electronics and Opto-Electronics with Semiconducting Carbon Nanotube Arrays**, ***M.B. Steiner***, IBM TJ Watson Research Center **INVITED**

While field-effect transistors made of single semiconducting carbon nanotubes have excellent electrical DC characteristics, the measurement of their AC characteristics is complicated and their output current is not sufficient for technological applications. Utilizing an array of semiconducting carbon nanotubes could resolve these problems. However, there are issues associated with the separation of carbon nanotubes with respect to the electronic type, their aligned assembly in high densities, as well as the scaling of device dimensions.

In this talk, I will present recent advancements with respect to the solution-assisted, electric-field driven assembly of highly separated (>99%) semiconducting carbon nanotubes into regular arrays on a device platform with embedded electrodes. The planar device platform is based on manufacturing processes known to the semiconductor industry and provides a basis for future enhancements of the carbon nanotube assembly and the scaling of critical device dimensions. Electrical transport measurements (AC and DC) of assembled carbon nanotube array transistors reveal intrinsic current gain cut-off frequencies of 150GHz and electrical current saturation behavior at a gate length of 100nm. The requirements for future applications of carbon nanotube array transistors in high-frequency electronics will be discussed.

In the second part of my talk, I will discuss high-resolution optical mapping of the internal electrostatic potential landscape of carbon nanotube array devices. Laser-excited photocurrent measurements provide insights into the physical principles of device operation and reveal performance-limiting local heterogeneities that cannot be detected with the electron microscope. The experiments deliver photocurrent images from the underside of nanotube-metal contacts and enable the direct measurement of the charge carrier transfer length at a nanotube-metal interface. Moreover, the external control of the electrostatic potential profile in carbon nanotube array devices by means of local metal electrodes is demonstrated. The results are important for the design and optimization of optoelectronic devices based on carbon nanotube arrays, such as polarized light detectors and emitters.

11:20am **NS+EN-TuM11 Observation of the Impact of Pseudospin Conservation in Carbon Nanotubes**, ***R. Tsuchikawa***, University of Central Florida, *Z. Zhang*, *X. Guo*, *J.C. Hone*, Columbia University, *M. Ishigami*, University of Central Florida

It has long been accepted that pseudospin conservation in metallic carbon nanotubes prevents backscattering by long-range potentials such as Coulomb potential. This unique property is expected to be valid only for metallic nanotubes [1]. Here, we have directly tested this yet untested theoretical result by measuring the impact of charged impurities on transport property of chiral-angle known carbon nanotubes. Single-walled carbon nanotubes (SWNTs) were grown to as long as a few hundred microns with minimal number of defects, followed by Rayleigh scattering spectroscopy to identify the chirality. In order to minimize the extrinsic impurities, electron transport measurements were performed in an ultra high vacuum environment after cleaning nanotubes down to atomic scale. Furthermore, we employed length-dependent resistance measurements to eliminate the impact of the metal-nanotube contact. Finally, transport property was measured at increasing coverage of cesium to determine the impact of charged impurities. Our results show chiral angle dependence of the impact of cesium and enable us to directly test the properties of pseudospin in carbon nanotubes.

1. P.L. McEuen, M. Bockrath, D.H. Cobden, Y.-G. Yoon, and S.G. Louie, Disorder, Pseudospin, and Backscattering in Carbon Nanotubes, Physical Review Letters, 83, 5098 (1999)

11:40am **NS+EN-TuM12 Properties and Application of Electronically Monodisperse Carbon Nanomaterials Functionalized with Nonionic Block Copolymers**, ***J.-W.T. Seo***, Northwestern University

Carbon nanomaterials, including carbon nanotubes and graphene, have garnered significant attention from the research community in recent years. In an effort to refine their properties and better integrate them into device structures, chemical functionalization methods have been employed including aqueous dispersion with ionic surfactants, proteins, and DNA. While these strategies have proven effective for tuning the optical properties of carbon nanomaterials, the residual charge from the ionic dispersants complicate efforts to utilize them in electronic and/or electrochemical technologies. In contrast, we demonstrate here that nonionic, amphiphilic block copolymers (e.g., Pluronics and Tetronics) are effective surfactants for graphene[i] and carbon nanotubes,[ii] thus yielding chemically and electronically monodisperse samples without spurious charged impurities.

Pluronics and Tetronics are biocompatible block copolymers that are composed of hydrophilic polyethylene and hydrophobic polypropylene oxide domains. By tuning the relative length of these domains, their dispersion efficiency for carbon nanomaterials can be tailored. For example, Pluronics possess the ability to sort semiconducting single-walled carbon nanotubes (SWCNTs) via density gradient ultracentrifugation with shorter hydrophobic domains resulting in higher purity levels. Furthermore, Pluronic F68 has shown pH-sensitive, switchable sorting affinity towards both metallic and semiconducting SWCNTs, thus providing a novel route for the production of electronically monodisperse SWCNTs that are encapsulated with biocompatible, nonionic species[iii]. In addition to biomedical applications, the nonionic character of these block copolymers yields more reliable and enhanced performance of SWCNT-based electronic and electrochemical devices such as thin film transistors and lithium ion batteries.

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