

Nanometer Structures

Room 308 - Session NS-TuM

Nanowires

Moderator: D.G. Cahill, University of Illinois, Urbana-Champaign

8:20am **NS-TuM1 Growth and Characterization of Single-Crystal ZnO Nanowires**, *Z. Zhu, T. Chen, Y. Gu, G. Neumark, R.M. Osgood Jr.*, Columbia University

One-dimensional ZnO nanowires have attracted increasing interest for both fundamental and applied studies of short-wavelength optoelectronic nanodevices. This talk reports a systematic study of effect of the variation of growth parameters, including growth temperature, growth time and catalyst (Au) film thickness, in determining the collective and individual structure of ZnO nanowires. Our single-crystal ZnO nanowires were grown on different-orientation silicon and sapphire substrates via vapor-phase transport. The synthesized ZnO nanowires were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), energy dispersive x-ray spectroscopy (EDS) and photoluminescence (PL) spectroscopy. Room-temperature photoluminescence spectra of the ZnO nanowires revealed a strong, narrow excitonic emission at ~ 380 nm and a very weak green emission band at ~ 508 nm. The full width at half maximum (FWHM) of the excitonic emission at ~ 380 nm was ~ 95 meV, indicating that the ZnO nanowires are of good optical quality. SEM measurements were made of ZnO nanowires grown on silicon substrates with Au films of different-coverage. The growth studies have shown that, as the Au-thin-film coverage decreases, the width and area density of the nanowires decreases while the length of the nanowires increases. In addition, the SEM measurements of the ZnO nanowires, grown at different substrate temperatures, show that the spatial uniformity of ZnO nanowires is strongly dependent on substrate temperature. Strategies of manipulating the spatial orientation of ZnO nanowires for practical applications are being explored by using nanofabrication techniques such as electron-beam lithography to pattern the substrates and build blocks to confine the growth of the ZnO nanowires; these studies will be reported in this talk.

8:40am **NS-TuM2 Growth and Characterization of ZnO Nanowires**, *J.B. Baxter, E.S. Aydil*, University of California, Santa Barbara

ZnO is a wide band gap semiconductor with applications in UV optoelectronics, transparent conducting oxide coatings, piezoelectronics, and photovoltaics. Nanostructured ZnO can exhibit quantum confinement effects and enable applications requiring high surface area such as sensors and dye sensitized solar cells. We have grown monodisperse ZnO nanowires by chemical vapor deposition (CVD) using the organometallic precursor zinc acetylacetonate ($\text{Zn}(\text{acac})_2$) in the presence of oxygen. Nanowire diameters depend on the growth conditions and range from 16 nm to 100 nm. The growth morphology depends sensitively on the substrate and the partial pressure of $\text{Zn}(\text{acac})_2$. On a-plane sapphire, nanowires grow epitaxially and perpendicular to the substrate in dense arrays and with in-plane rotational order. X-ray diffraction pole figures confirm the epitaxial relationship $\text{ZnO}(0001) \parallel \text{Al}_2\text{O}_3(11\bar{2}0)$ and $\text{ZnO}(11\bar{2}0) \parallel \text{Al}_2\text{O}_3(10\bar{1}1)$. Conversely, nanowires grow on c-plane sapphire in one of three directions relative to the substrate owing to $\text{ZnO}(0001) \parallel \text{Al}_2\text{O}_3(10\bar{1}1)$ epitaxy and the trigonal symmetry of the substrate. Controlled sublimation and delivery of the solid precursor is challenging. However, we are improving our ability to control nanowire growth by studying the evaporation and decomposition of $\text{Zn}(\text{acac})_2$ using thermogravimetric analysis and mass spectrometry and by monitoring the presence of the $\text{Zn}(\text{acac})_2$ with in situ Fourier transform infrared (FTIR) spectroscopy. Dense ZnO nanowires with high surface area can be grown on various oxide substrates, making them suitable for replacing the mesoporous semiconductor in dye sensitized solar cells. Single crystal ZnO nanowires offer improved conduction pathways compared to sintered nanoparticles used currently, where electron transport occurs by a hopping mechanism.

9:00am **NS-TuM3 Structure, Defect and Cathodoluminescence Studies of GaN Nanorods and Nanowires**, *L.C. Chen*, National Taiwan University, Taiwan; *C.S. Shen, S.C. Shi*, National Taiwan University; *S. Dhara, C.T. Wu, K.H. Chen*, Academia Sinica, Taiwan; *C.W. Hsu, C.C. Chen*, National Taiwan Normal University

Single-crystalline GaN and related 1D nanostructures, specifically, binary InN, AlN along with their ternary $\text{In}_x\text{Ga}_{1-x}\text{N}$ and $\text{In}_x\text{Al}_{1-x}\text{N}$ counterparts have been successfully grown by catalytic

chemical vapor deposition. Their structure and optical properties are investigated by scanning and transmission electron microscopy, Raman, photoluminescence (PL) as well as cathodoluminescence (CL) techniques. Diameter and position selective growth of these 1D nitride nanostructures has been demonstrated by pre-treatment of the substrate surface with size-controlled catalyst. Oriented growth of the nanorods was also obtained under hetero- or homo-epitaxial conditions. While PL measurements usually give spectral data from numerous nanowires and nanorods with a broad distribution of diameter, the CL measurements (from room temperature down to 4 K) can easily be performed on single nanowire or nanorod. A higher CL peak position of individual GaN nanorod than that of bulk GaN film was observed, indicating the presence of strain in the pristine nanorod, which is also confirmed by X-ray diffraction analyses. In addition, a blue shift of CL peak position with decreasing the diameter of GaN nanorod was noticed. However, the magnitude of the peak shift is much more pronounced than that estimated from quantum confinement. Finally, Ga³⁺ ions implantation of these GaN 1D nanostructures has been studied using 50-keV Ga³⁺ focused ion beam. Phase transformation and defect structure evolution as a function of irradiated ion-beam fluence is also investigated by electron-microscopy-based techniques.

9:20am **NS-TuM4 Onset of Nanowire Growth by Vapor-Liquid-Solid (VLS) Epitaxy**, *J.W. Dailey, J.L. Taraci, T. Michael, J.C. Thorp, S.T. Picraux*, Arizona State University

We report on CVD growth of Ge and Si nanowires on Si substrates by the Vapor Liquid Solid (VLS) technique. While many groups have formed random clusters of Si nanowires at high pressures by VLS, relatively little effort has been directed at the controlled CVD growth of epitaxial arrays of nanopillars or nanowires directly onto Si substrates. In our studies Au nanodots are formed by UHV evaporation on hydrogen terminated Si (100) and (111) substrates. Subsequent selective area growth is carried out using digermane or disilane at pressures from 1×10^{-2} to 1×10^{-5} T and temperatures from 400 to 600 C. At the lower pressures (representative of gas phase MBE) we observe the growth of Ge nanopillars that nucleate at the AuSi eutectic and grow vertically and laterally, undergoing coalescence as growth continues. RBS and ion channeling are used to establish the VLS substrate orientation and temperature dependent kinetics of the Ge nanopillar growth, and SEM elucidates the morphological evolution of the nanopillars. At pressures above 10^{-4} T we observe an abrupt change in the nature of the growth from a relatively slow nanopillar growth to a much more rapid nanowire growth. The nanowires are distinguished by long narrow axial growth structures with much slower lateral growth. The transition from nanopillar to nanowire growth is interpreted in terms of a nucleation-limited process. Due to the small lateral dimensions (10 to 50 nm) of these 3-D structures lateral strain relief is expected to occur and large lattice mismatches should be accommodated without defects, in contrast to large area heteroepitaxy. These CVD nanoscale structures could form the basis for new in situ synthesis of 3-D Si device structures on Si substrates.

9:40am **NS-TuM5 Functional Semiconductor Nanowires and Their Optical Properties**, *P. Yang*, University of California, Berkeley **INVITED**

Nanowires are of both fundamental and technological interest. They represent the critical components in the potential nanoscale electronic and photonic device applications. In this talk, I will introduce the vapor-liquid-solid crystal growth mechanism for the general synthesis of nanowires of different compositions, sizes, orientation and doping profile. Particularly, synthesis and organization of different types of heterostructured nanowires will be discussed. Wide band gap semiconductor nanostructures with near-cylindrical geometry and large dielectric constants exhibit two-dimensional ultraviolet and visible photonic confinement (i.e. waveguiding). Combined with optical gain, the waveguiding behavior facilitates highly directional lasing at room temperature in controlled-growth nanowires with suitable resonant feedback. The nanowire optical emission has been studied in detail using high-resolution optical microscopy. The waveguiding behavior of individual zinc oxide (ZnO, GaN) nanowires depends on the wavelength of the emitted light and the directional coupling of the photoluminescence (PL) to the emission dipoles of the nanowire. Pumping at high pulse intensity leads to the transition from spontaneous to stimulated emission, and analysis of the polarization, linewidth, and spacing of the spectral features facilitates identification of the transverse and longitudinal cavity modes and their gain properties. The observation of lasing action in arrayed and isolated ZnO/GaN nanowires without requiring fabrication of mirrors suggests the single-crystalline, well-faceted nanowires can indeed function as effective resonance

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cavities. This concept of using well-cleaved nanowires as natural optical cavities may be extendable to many other different semiconductor systems. @FootnoteText@ @footnote 1@ Y. Wu, R. Fan, P. Yang, Nanolett, 2, 83, 2002. @footnote 2@ M. Huang, S. Mao, H. Feick, H. Yan, Y. Wu, H. Kind, E. Weber, R. Russo, P. Yang, Science, 292, 1897, 2001. @footnote 3@ J. Johnson, H. J. Choi, K. P. Knutsen, R. D. Schaller, R. J. Saykally, P. Yang, Nature Materials, 1, 101, 2002. @footnote 4@ J. Johnson, H. Yan, R. Schaller, L. Haber, R. Saykally, P. Yang, J. Phys. Chem. B, 105, 11387, 2001.

10:20am **NS-TuM7 Mo@sub 3@Se@sub 3@ Nanowires - Mechanical and Electrical Properties at the Nanoscale, A. Heidelberg**, Trinity College Dublin, Ireland; *J.W. Schultze*, Heinrich-Heine-Universität Düsseldorf, Germany; *G. Staikov*, Forschungszentrum Jülich, Germany; *J.J. Boland*, Trinity College Dublin, Ireland

Low dimensional organic and inorganic materials like nanowires and nanotubes have attracted much interest as potential building blocks for nanotechnology. This interest can be traced to the novel structural and electronic properties of these materials. Here we describe a study that measures the electronic and mechanical properties of the inorganic polymer (LiMo@sub 3@Se@sub 3@)@sub n@ together with nanowire-networks that have been synthesized by exchanging the Li-counterion with different alkylammonium- and pyridinium-ligands. (LiMo@sub 3@Se@sub 3@)@sub n@ forms quasi-1D crystals and is structurally related to the Chevrel phases. It can be viewed as a condensation polymer of Mo@sub 3@Se@sub 3@ units. The crystals can be dissolved in polar solvents with @epsilon@ > 45. In these solvents the crystals disassemble into single nanowires with a diameter of 0.6 nm (from crystal data and TEM) and bundles of nanowires, depending on the solutions concentration. From solution, single nanowires, bundles of nanowires or films of nanowires can be cast on various substrates. Both, the wires themselves as well as the nanowire films are highly conductive but susceptible to electrical degradation (oxidation) in air. The ion exchanged wires form self assembled networks with an inter-wire spacing determined by the length of the side chain of the alkylammonium- and pyridinium-ligands. Conductivity measurements on these nanowire networks at different temperatures and oxidation times show that conduction is activated and occurs via a percolation mechanism. The mechanical properties of single nanowires or bundles were studied using a SPM-nanomaniplator. This instrument allows us to controllably apply forces (μN -nN range) to supported Mo@sub 3@Se@sub 3@-nanowires to effect nanoscale manipulations. Using the lateral force data of the manipulations, the mechanical properties like Youngs modulus and tensile strength of the wires can be measured.

10:40am **NS-TuM8 Defect Mediated Electronic Transport in Nano and Molecular Wires, D.A. Bonnell, S. Kalinin, M. Freitag, A.T. Johnson**, University of Pennsylvania

Any rational approach to nanostructure design necessitates a fundamental understanding of the properties of the constituents, as well as collective behavior of ensembles. We have developed 2 new approaches to measuring local electromagnetic properties based on scanning probes that can be applied to nano and molecular wires, Scanning Impedance Microscopy and Nano Impedance Spectroscopy. These approaches access the frequency dependence of electronic transport over 3-6 orders of magnitude, depending on experimental conditions. The frequency dependence can be used to determine mechanisms of electronic transport, particularly the processes that occur at defects. We demonstrate this approach by determining the local electronic structures of individual defects in single walled carbon nanotubes. We then generalize to nanowires and molecular wires.

11:00am **NS-TuM9 Electronic Structure and Excited States of One-dimensional Polydiacetylene Nanowire, M. Akai-Kasaya, K. Shimizu, A. Saito, M. Aono, Y. Kuwahara**, Osaka University and SORST JST, Japan

The polydiacetylene (PDA) nanowire can be fabricated at designated positions by using a STM probe tip on a self-assembled monomolecular (SAM) layer. @footnote 1@ The fabricated PDA wire grows out in a straight line and extends to a sub-micrometer length on the surface. The fully extended conjugated backbone of the PDA is not only expected to function as an electrically conducting nanowire but is also interesting in terms of exploring physics in one-dimensional (1D) systems. In this work, the density of states of individual polymers and constituent monomers were studied by STS. The STS spectrum delineating the density of states of PDA wire clearly reveals the theoretically predicted @pi@-band and band edge singularities of the 1D conjugated polymer. We have also observed a fascinating spectrum with a narrow gap, which is suggested to be due to the existence

of the charge-carrying polaron states on a polymer backbone. Furthermore, we demonstrated that an excited state took place in an isolated polymer nanowire following the polymerization. The voltage pulse initiates additive polymerization, which proceeds instantaneously to both sides of the monomer array on the SAM layer. Before and after polymerization within the disabled feedback loop, the tunneling current shows the accountable difference due to the steady-state current on the monomer and derived polymer, respectively. However, the anomalous current, which often continues for few hundred micro-seconds, has been observed simultaneously with inception of the polymerization. We have estimated statistically the time of onset and duration of the current and correlation with the length of the derived polymer wire. And then, it can be concluded that the detected anomalous current results from the vibrational excitation states of a derived molecular nanowire. These results are remarkable and interesting in terms of one molecular science. @FootnoteText@ @footnote 1@ Y. Okawa and M. Aono, Nature 409, 683 (2001).

11:20am **NS-TuM10 STM and DFT Study of Gadolinium Silicide on Si(100), B.C. Harrison**, University of North Carolina at Chapel Hill, Ireland; *J.J. Boland*, Trinity College Dublin, Ireland

The fabrication and characterization of low-dimensional nanoscale structures is motivated by the desire to produce materials and devices with novel optical, structural, and electronic properties. Due to the difficulties in nanoscale fabrication by a top-down approach, self-assembly of nanoscale materials represent an attractive alternative. Rare earth silicide on the Si(100) surface is one such system that has attracted significant interest over the past several years. Nanostructures of various silicides @footnote 1,2,3@ have been formed with high aspect ratios, micrometer length scales, large mechanical strengths, and metallic character; all of which make them potential candidates for nanoscale interconnects or device components. However, these nanowires cannot be successfully used in electronic circuits until the morphology and placement of wires are controlled. This study focuses on Gadolinium Silicide (GdSi@sub 2@) on Si(100) since this silicide forms nanowires and has the smallest lattice constant mismatch in the wire growth direction of any of the available rare earth silicides at growth temperatures. Scanning Tunneling Microscopy data and DFT calculations results are coupled to determine the morphology of the various phases of GdSi@sub 2@ on the Si(100) surface. Furthermore, STM images are acquired from room temperature to wire-growth temperatures in order to study the atomic structure and growth processes of the initial wetting layer and nanowires themselves. At least three forms of the wetting layer and two forms of wires will be discussed in connection with an overall surface phase diagram for GdSi@sub 2@ on Si(100). @FootnoteText@ @footnote 1@ Chen, Y.; Ohlberg, D. A. A.; Williams, S. J. Appl. Phys. 2002, 91, 3213. @footnote 2@ Chen, Y.; Ohlberg, D. A. A.; Medeiros-Riberio, G.; Chang, Y. A.; Williams, S. Appl. Phys. Lett. 2000, 76, 4004. @footnote 3@ Nogami, J.; Liu, B. Z.; Katkov, M. V.; Ohbuchi, C.; Birge, N. O. Phys. Rev. B 2001, 63, 233305-1.

11:40am **NS-TuM11 Theoretical Calculation of the Thermal Conductivity of Semiconducting Nanowires, N. Mingo, L. Yang**, NASA-Ames Research Center

An atomistic Green function theoretical formalism to compute phonon transport in nanostructures will be presented, and its application to several different problems will be discussed. In particular, we present calculations of the thermal conductivity of Si and Ge nanowires, and compare these with some experimental results [D. Li et al., submitted]. One important problem that has not yet been extensively studied in an atomistic framework, is that of ballistic vs. diffusive phonon transport. Using our atomistic Green function approach, we study the transition from ballistic to diffusive phonon transport, occurring as the system's length increases. The way in which this transition takes place is largely determined by properties of its boundary. We will discuss the ballistic-diffusive transition in terms of atomic properties of the wire and its coating. Differences between (111) and (110) orientated nanowires are shown to be of more importance in the ballistic regime than in the diffusive one. Finally, a two parameter model, with the parameters depending only on bulk material properties, is also derived. Using this method we obtained good predictive calculations of the thermal conductivity of Si nanowires. The method employs the full phonon dispersion relations of bulk Si. The relative importance of specific nanowire modes not present in bulk, as the system's size becomes smaller, will be discussed. The results and methods presented offer an exciting new range of possibilities in the study and development of thermal transport through nanosized devices.

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