Tuesday Morning, October 19, 2010

Nanometer-scale Science and Technology
Room: La Cienega - Session NS-TuM

Nanomanufacturing and Nanomachines
Moderator: M. Hersam, Northwestern University

8:00am **NS-TuM1 Nanomanufacturing Processes using Mechanosynthesis Applications**, ***S.L. Sullivan***, NanoSource Inc.

Quality, production capacity and production cost have been identified as the current barriers to the implementation of carbon nanotubes and nanofibers within the industrial markets and military applications where such materials offer superior performance benefits. Significant use of nanotubes and nanofibers will require substantial increases in production volume coupled with decreases in production cost of < $ 15/Kg. Based on low cost, high-volume, high yield, and the ability to highly control diameter, length and chirality, a Mechanosynthesis process was selected as the most viable approach for a scalable, top down mass manufacturing process of nanoscale structures such as nanoparticles, nanotubes and nanofibers that are continuous.

Index Terms- Mechanosynthesis, nanomanufacturing, nanoimprinting, nanofibers, material science.

8:20am **NS-TuM2 Enabling Surface Patterning on Polyhedral and Curved Nanoparticles**, ***J.-H. Cho***, Los Alamos National Laboratory, *T. James, D. Gracias*, Johns Hopkins University

It is well known that surface patterning on three dimensional (3D) nanostructures can alter their physical and chemical properties. However, present day nanoparticles such as nanowires and nanopolyhedra have limited to no surface patterning. Lithographic processes enable precise patterning and are very well developed. There are several nanolithographic techniques such as electron beam (e-beam), imprint, and dip pen lithography that can enable patterning, but in an inherently two dimensional manner.

In this talk, we describe strategies to curve and rotate precisely patterned thin film templates to form 3D nanostructures such as cubes, pyramids, tubes, scrolls and talons. The highlight of the approach is that the process leverages already existing nanolithographic techniques and enables structures to be formed with any desired surface patterns in all three dimensions; a line width resolution of 10 nm was achieved.

We utilized multiple layers of electron beam lithography to pattern 2D templates. Patterns with homogeneous (pores in nickel panels) or dissimilar materials (e.g. gold lines on nickel or alumina) were defined. Curvature of hingeless templates and rotation of hinged panels was achieved by triggering grain coalescence in tin (Sn). Polyhedral particles ranging in size from 100-900 nm and surface patterning of 15 nm could be achieved. In addition, curved nanostructures with both homogeneous (rings, tubes) and variable (spirals, talons) radii of curvature could be formed.

Our demonstration of patterning of self-assembly of precisely patterned polyhedral and curved nanoparticles has material versatility and we believe that this strategy can be utilized to integrate optical, electronic and biological elements on the surfaces of nanoparticles with unprecedented precision and in all three dimensions for a range of applications.

8:40am **NS-TuM3 Atomic Precision Fabrication Using Patterned Si Atomic Layer Epitaxy: Processing Capabilities, Throughput Limitations, and Applications**, ***J.N. Randall***, *J.B. Ballard, J.R. Von Ehr, J. Alexander, R. Saini,* Zyvex Labs, *J.W. Lyding,* Univ. of Illinois at Urbana-Champaign, *R.M. Wallace, Y.J. Chabal,* Univ. of Texas at Dallas, *R.M. Silver, J. Gorman,* National Inst. of Standards and Tech., *N. Sarkar,* Univ. of Waterloo, Canada, *T. Toth-Fejel*, General Dynamics **INVITED**

Atomically precise Si fabrication technology is being pursued via atomic-precision, H-depassivation lithography with a scanning tunneling microscope (STM) and silicon atomic layer epitaxy (ALE). The details of this process and progress towards its realization are published elsewhere. In this presentation we will cover the expected process capabilities, throughput limitations, applications that will be feasible in spite of these limitations, extensions of the processing capabilities, and paths to scaleup of the throughput. Initially the fabrication process will involve simply patterned homo-epitaxy of Si on Si surfaces, but will allow arbitrary three dimensional structures with some design rules imposed by the Si lattice.The limitations imposed by the physics of the H depassivation lithography and the need for repeated patterning is the principal process bottleneck and leads to estimations of a cost per unit volume of atomically precise fabricated material that seems extremely high. However, the ability to create structures with atomic precision will enable very valuable applications and products that can be cost effectively manufactured in the relatively near term. This process, which can be conceived of as spatially controlled deprotection, appears to be general enough to adapt to the large number of materials that may be deposited with ALE or atomic layer deposition (ALD). Further, there are clear paths to scaling up the process via MEMS-based STM scanner arrays that would significantly widen the range of products and applications resulting from this Atomically Precise Manufacturing technology.

This material is based upon work supported by the Defense Advanced Research Project Agency (DARPA) and Space and Naval Warfare Center, San Diego (SPAWARSYSCEN-SD) under contract N66001-08-C-2040. It is also supported by a grant from the Emerging Technology Fund of the State of Texas to the Atomically Precise Manufacturing Consortium.

9:20am **NS-TuM5 Axial Ge/Si Nanowire Heterostructures: Synthesis and Asymmetric Band-gap Engineered Tunnel FETs**, ***S.A. Dayeh***, Los Alamos National Laboratory, *J. Huang, A. Gin,* Sandia National Laboratories, *S.T. Picraux*, Los Alamos National Laboratory

While new materials and device concepts are being developed to extend CMOS device scaling beyond the 22 nm node, the potential of combining Si/Ge heterostructured materials with the dimensionality of semiconductor nanowires (NWs) remains to be explored. The vapor-liquid-solid (VLS) mechanism allows modulation of doping and alloy composition in the axial NW direction which is the transport direction for NW FETs. This provides an additional degree of freedom for energy band-edge engineering in the transport direction which is difficult to access in planar devices. Such unique aspect of semiconductor nanowires when added to Ge compatibility for integration with Si technology, makes Ge/Si axial NW heterostructures advantageous over other existing material and device possibilities, in particular for tunnel FETs.

This work reports on two significant advances in the area of heterostructure nanowires and tunnel FETs: (i) the realization of 100 % compositionally modulated Si/Ge axial heterostructure nanowires with lengths suitable for device fabrication and (ii) the design and implementation of Schottky barrier tunnel FETs on these nanowires for high-on currents and suppressed ambipolar behavior. A growth procedure was devised to eliminate Au diffusion on the NW sidewalls and minimize random kinking in the heterostructured NWs as deduced from detailed electron microscopy analysis. Our prototype devices resulted in a current drive in excess of 100 $\mu A/\mu m$ ($I/\pi D$) and 10^5 I_{on}/I_{off} ratios over a wide range of source-drain biases, thus exceeding earlier performance results in the literature of tunnel FET devices made of semiconductor nanowires and carbon nanotubes by ~ 2-3 orders of magnitude. These results demonstrate the potential of such asymmetric heterostructures (both in the semiconductor channel and metal-semiconductor barrier heights) for low-power and high performance electronics.

9:40am **NS-TuM6 Direct Writing of Polymers using a Heated Probe for Patterning Nanoparticles and Graphene**, ***W.-K. Lee***, *J.A. Robinson, A.R. Laracuente,* Naval Research Laboratory, *Z. Dai, W.P. King,* University of Illinois at Urbana-Champaign, *P.E. Sheehan*, Naval Research Laboratory

In thermal Dip Pen Nanolithography (tDPN), a heatable AFM cantilever regulates the deposition of an ink through controlled melting, much like a nanoscale soldering iron. Control over writing is exceptional—deposition may be turned on or off and the deposition rate easily changed without breaking surface contact. tDPN has been successful at depositing polymers ranging from semiconductors to insulators at speeds up to 200 μm/s. Recently, we developed the technique depositing polymer-nanoparticle composites. Nanoparticles and nanoparticles–polymer composites may offer many new capabilities that could greatly advance nanoelectronics, data storage, biosensors, and optical imaging applications. With tDPN, we could deposit with nanoscale precision a wide range of polymers (PMMA, P(VDF-TrFE), polyethylene) that contain nanoparticles or small molecules. An oxygen plasma can remove the polymer to reveal evenly dispersed nanoparticles or, for some combinations, precisely-placed 10 nm wide rows of nanoparticles.

Another substrate, a single layer of graphene on a SiO_2, was also used to deposit polymers by tDPN. We used the deposited polymer on graphene as an etch mask to pattern graphene nanoribbons (GNRs). Background graphene was then either etched by oxygen plasma to expose SiO_2 or modified by graphene fluoride to form an insulating substrate. The electrical measurements of nanopatterned graphene structures will also be presented.

10:40am **NS-TuM9 Understanding and Controlling Rotation at the Single-Molecule Level: Turning Rotors into Motors**, ***H.L. Tierney****, *A.D. Jewell, A.E. Baber, E.V. Iski, E.C.H. Sykes*, Tufts University

While molecular machines driven by chemical, light or thermal energies can be found throughout nature, little progress has been made toward creating synthetic counterparts. The gap between nature and nanotechnology remains due to the limited fundamental understanding of the transfer of energy to mechanical motion at the nanoscale. Understanding and actuating the rotation of individual molecules on surfaces is a crucial step towards the development of nanoscale devices such as fluid pumps, sensors, delay lines, and microwave signaling applications. Towards this end we have used a group of small molecules in order to understand the fundamental aspects of molecular rotation. Thioethers constitute a simple, robust system with which molecular rotation can be actuated thermally, mechanically and electrically, and can be studied using scanning tunneling microscopy (STM) as a function of molecular chemistry and proximity of neighboring molecules. Interestingly, the thermal onset to rotation was found to be nearly identical for studied thioether molecules with alkyl tails of two carbons or more. It is proposed that this plateau in thermal onset was due to an interplay between degrees of freedom in the alkyl tail vs. the S-metal bond length. While small amounts of thermal energy are capable of inducing rotation, thermodynamics dictates that thermal energy alone cannot be used to perform useful work in the absence of a temperature gradient. Therefore, for molecules to meet their full potential as components in molecular machines, methods for coupling them to external sources of energy that selectively excite the desired motions must be devised. To this end, we have studied using an electrical current to rotate individual dibutyl sulfide molecules on command. For these studies the source of energy is supplied via high energy electrons from the STM tip. By monitoring the rate of rotation as a function of tunneling electron energy (action spectroscopy) we have demonstrated that the rotors can be driven electrically via a mechanism that involves excitation of a C-H stretch. Finally, using theoretical methods the minimum energy adsorption site was determined and the mechanism of rotation was elucidated for the simplest thioether, dimethyl sulfide. These theoretical results indicate that the rotation of a small, simple molecule is actually rather complex; as the CH_3 groups of dimethyl sulfide rotate around the Au−S bond, the central S atom precesses around a surface Au atom.

11:00am **NS-TuM10 Atomic Layer Deposition on Self-Assembled Block Copolymer Films**, *Q. Peng, Y.-C. Tseng,* ***S.B. Darling****, J.W. Elam*, Argonne National Laboratory

We establish a new method for preparing ordered nanoscale patterns of various materials with tunable domain sizes by applying atomic layer deposition onto block copolymer thin films. The mechanism is based on the selective interaction of the ALD precursors with moieties in one of the polymer blocks. Well aligned, patterned Al_2O_3 and TiO_2 stripes with controllable dimensions were fabricated by applying ALD onto PS-*b*-PMMA block copolymer templates. Moreover, due to the self-limited cyclic deposition nature of ALD, a seed layer generated from Al_2O_3 ALD provides a secondary selective chemistry, which in turn enables a far broader suite of materials to be patterned into the PMMA domains. For example, ZnO and W nucleate easily on the PMMA-Al-OH domains formed from one cycle of Al_2O_3 ALD. By carefully designing block copolymers and selecting ALD parameters, patterned designer materials with controlled size, center-to-center space, and composition could be synthesized onto a broad range of substrates.

11:20am **NS-TuM11 In Control of Molecular Motion** ***From Molecular Motors to Nano-Machines****,* ***B.L. Feringa***, The University of Groningen, the Netherlands **INVITED**

Inspired by Nature we design nano-scale systems in which the control of dynamic properties of molecules is coupled to specific functions. Molecular machines ultimately require control over structure, organization and function of multi-component molecular assemblies at different hierarchical levels. Major challenges are the integration of kinetic driven processes in multifunctional molecular systems and control over translational and rotary motion.

Molecular switches and motors offer ample opportunity to control functions in a dynamic way. Following the development of the first light-driven unidirectional molecular motor, the focus is now on the control of dynamic functions in more complex systems as well as autonomous motion. Synthetic approaches to various molecular switches and motors and the construction of integrated systems featuring trigger and motor elements are discussed.

Specific challenges that we address are the acceleration of molecular rotary motors and the construction of a nanoscale “windmill park” powered by light. Recent advances in the design of new generation motors that allow the increase of the speed of rotation over a million fold are presented. Furthermore the design of molecular motors in which the rotary direction can be reversed, a molecular crankshaft and brake and molecular transmission phenomena are discussed. Besides rotary motion induced by light, we present unique molecular motors that run on a chemical fuel and discuss our attempts to achieve autonomous motion.

***** Morton S. Traum Award Finalist

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