

Thursday Morning, November 3, 2011

Nanometer-scale Science and Technology Division

Room: 203 - Session NS-ThM

Molecular Assembly and Devices

Moderator: W. Gao, Brigham and Women's Hospital and Harvard Medical School

8:20am **NS-ThM2 Chemical Modification and Patterning of Self Assembled Monolayers using Scanning Electron and Ion-Beam Lithography**, *M.J. Perez Roldan, C. Pascual Garcia, G. Marchesini, D. Gilliland, G. Ceccone, P. Colpo, F.J. Rossi*, European Commission, JRC Institute for Health And Consumer Protection, Italy

We present chemical modification of self assembled monolayers (SAMs) using electron and ion-beam lithographies. We used thiolated polyethylene oxide (PEO) SAMs on gold to fabricate chemically contrasting patterns at the nanoscale. Patterned surfaces were characterized by X-ray photoelectron spectroscopy (XPS), time of flight-secondary ion mass spectrometry (ToF-SIMS). Results showed a chemical modification of surfaces patterned by means of electron beam (e-beam) lithography and a removal of PEO SAMs on the areas treated with the ion beam. The chemical modification of PEO SAMs converted the non-fouling surfaces on fouling surfaces.

8:40am **NS-ThM3 Interlocking Pinwheel Chains Formed by Self Assembly of Aromatic Cyanides**, *M. Luo, W. Lu, E. Chu, D. Kim, Z. Cheng, D. Sun, K. Cohen, Y. Zhu, J. Wyrick*, University of California, Riverside, *T.L. Einstein*, University of Maryland, College Park, *L. Bartels*, University of California, Riverside

As part of a bottom-up strategy, molecular self assembly can be a promising technique to create surface patterns with ultimately small feature sizes in an economic efficient fashion. Understanding of the factors which guide molecules into different patterns thus become an important goal for prediction and control of molecular patterns structures.

Here we present the formation of interlocked arrays ('gear chains') of pinwheels through self-assembly of 3-phenyl-propynenitrile (PPN) molecules on a Cu(111) surface. Variable temperature scanning tunneling microscopy (STM) reveals upon molecular deposition a pattern of small hexagonal features, which coalesce into sequences of larger, interlocking pinwheel-shaped structures. The pinwheels have an outer diameter as large as ~4nm. The driving force of this entropically disfavored pinwheel formation is discussed.

9:00am **NS-ThM4 Electronics and Mechanics of Single Molecule Circuits**, *L. Venkataraman*, Columbia University **INVITED**

Understanding and controlling electron transfer across metal/organic interfaces is of critical importance to the field of organic electronics and photovoltaics. Single molecule devices offer an ideal test bed for probing charge transfer details at these interfaces. Results from these single-molecule measurements can be directly related directly theoretical models, unlike measurements at the ensemble level. The ability to fabricate single molecule devices and probe electron transfer reliably and reproducibly has enabled us to study and model transport through them.

In this talk, I will review the scanning tunneling microscope break-junction technique we use to measure electronic transport through single molecule junctions. I will discuss our measurements using novel metal-molecule link chemistries, including amines, phosphines[1] and results from recent work using tri-methyl tin linkers, which yield direct Au-C coupled single molecule junctions[2]. I will show how the intrinsic molecular properties influence measured single molecule conductance and bond rupture forces[3]. Finally, I will show how a mechanically controlled binary single molecule switch can be created using bipyridine molecules[4].

[1] Y. S. Park et al., *J. Am. Chem. Soc.* 129, 15768 (2007).

[2] Z.-L. Cheng et al., *Nat. Nano.* In Press (2011).

[3] M. Frei et al., *Nano Lett.* 11, 1518 (2011).

[4] S. Y. Quek et al., *Nat. Nano.* 4, 230 (2009).

9:40am **NS-ThM6 Complex Rotation Mechanisms of a Molecular Machine Probed by STM**, *H. Kersell, U.G.E. Perera, Y. Zhang*, Ohio University, *C. Joachim, G. Rapenne, G. Vives, X. Bouju*, CNRS, Cemes, France, *S.-W. Hla*, Ohio University

The complex rotation of a ruthenium based double-decker molecular rotor is resolved via ultrahigh vacuum low temperature scanning tunneling microscopy. The study was performed at temperatures of 4.2 K and 77 K on

a Au(111) substrate. Inelastic electron tunneling (IET) was utilized to induce stepwise rotation of the molecule with respect to the surface. Subsequent rates of molecular switching, induced via tunneling currents, display sets of discrete energy minima with respect to the molecular stator and to the surface. The molecular rotator is composed of a set of semi-rigid arms whose non-rigid components, upon IET induced rotation, are observed to change conformation to the particular energy minima of the rotor. The resulting STM images were compared to calculated images of the same molecule. Additionally, the rotator was dissociated, revealing an intact stator adsorbed on the Au(111) surface. We acknowledge the financial support of US-DOE; DE-FG02-02ER46012, and NSF-PIRE; OISE 0730257 grants.

10:40am **NS-ThM9 Self-Assembled Double Strand DNA Monolayers as Spin Filters**, *Z. Xie, S.R. Cohen, T.Z. Markus, R. Naaman*, Weizmann Institute of Science, Rehovot Israel

Spin control provides new and interesting opportunities for control and study of the factors governing electron transport. Recent work by Naaman and co-workers has shown that self-assembled monolayers of double stranded DNA (ds-DNA) can act as a spin filter for electrons photoemitted from a gold substrate.[1,2] This phenomenon depends on the helicity of the ds-DNA, which leads to spin polarization and consequent capture of filtered electrons that tunnel back to the substrate. In this work, this effect is investigated for electron flow between two electrodes, a bottom Ni electrode to which one strand of the DNA is bound, and a top gold nanoparticle electrode which serves to identify the ds-DNA and provide good electrical contact through binding to the complementary strand. The current characteristics are measured by conductive scanning probe microscopy, as applied in a previous study of electron transport in DNA monolayers.[3] A magnetic field of approximately 0.3 T at the surface is provided by a permanent magnet placed below the sample. The results are consistent with the photoemission work, namely marked differences in the current flow depending on magnetic field alignment. Furthermore, the effect depends on length of DNA chain, with longer chains providing a more significant effect relative to shorter ones. These experimental findings, together with a physical model will be presented.

[1] Goehler, et al, *Science* 331, p. 894 (2011).

[2] Ray, et al, *Phys. Rev. Lett.*, 96, 03101 (2006).

[3] Nogues et al, *J. Phys. Chem. B* 110, 8910 (2006).

11:00am **NS-ThM10 Controllable Phase Transition Using a Probing Tip**, *Q. Li*, Oak Ridge National Laboratory

Molecular Self-assembled monolayers have applications in many different fields, such as sensing, lubrication and molecular electronics. In our study, a movie containing more than 50 STM images is acquired to investigate the dynamic behavior of the phenyl-acetylene molecular assembly process on Au(111) surface at LN2 temperature. Besides that, we found the phenyl-acetylene molecules are very sensitive to the polarity of the bias voltage. Therefore, phase transition between molecular ordered and disordered structure can be controllably achieved by applying positive or negative bias voltage. Systematically study of the phase transition process turned out it may be related to the charging effect of the molecules.

11:20am **NS-ThM11 How Size, Shape, and Bond Strain Affect Electronic Structure in sp³ Carbon-Cage Molecules**, *T.M. Willey, J.R.I. Lee*, Lawrence Livermore National Lab, *L. Landt, D. Wolter*, Technische Univ. Berlin, Germany, *M. Bagge-Hansen*, Lawrence Livermore National Lab, *P.R. Schreiner, A.A. Fokin, B.A. Tkachenko, N.A. Fokina*, Justus-Liebig Univ. Giessen, Germany, *T. van Buuren*, Lawrence Livermore National Lab, *D. Brehmer*, Stanford Synchrotron Light Source

Novel nanocarbons such as fullerenes, nanotubes, graphene, and nanodiamond reside at the cutting edge of nanoscience and technology. This paper presents a fundamental study of how size, shape, chemical functionalization, and bond strain affect electronic structure in several benchmark series of chemically pure, novel carbon-cage compounds ranging from diamondoids (a fully sp³ form of nanodiamond) to cubane. Size and shape are studied with the diamondoid series from adamantane to hexamantane, where the observed gap changes are primarily due to evolution in occupied states, as measured with photoelectron spectroscopy (XPS & UPS). Bond strain is studied with dodecahedrane, octahedrane, and cubane, where increasing bond strain leads to two major changes in the near-edge x-ray absorption fine structure (NEXAFS) spectra. First, a broad C-C σ^* resonance in the absorption splits into two more narrow and intense resonances with increasing strain. Second, the first manifold of states previously associated with tertiary C-H σ^* in the diamondoid series appears to broaden and shift to lower energy. This feature is more than twice as

intense in cubane as octadecane, even though these two molecules have similar stoichiometries ($C_{12}H_{12}$ vs. C_8H_8). We attribute the additional intensity to π^* states, indicating a high degree of p interaction between parallel C-C bonds in the cubane.

11:40am **NS-ThM12 Effect of Acetylene Concentration and Thermal Ramp Rate on the Growth of Spin-capable Carbon Nanotube Forests.**
K.H. Lee, D. Burk, L.J. Overzet, G.S. Lee, The University of Texas at Dallas

Spin-capable multi-walled carbon nanotube (MWCNT) forests that can form webs, sheets, and yarns provide a promising means for advancing various technologies [1-4]. The important factors enabling the growth of the spin-capable forests are still not well understood. Growing spin-capable CNT forests depends on several growth factors such as the catalyst film thickness, the growth temperature, and the carrier and reactant gases [5-9]. Other factors still remain to be investigated more thoroughly. These include the flow rate (or ratio) of the reactant gas, the reactant gas species, and the pressure.

Herein we show how both the spinning capability and morphology of MWCNT forests are changed significantly by controlling the acetylene (C_2H_2) concentration and the thermal ramp rate. The acetylene gas flow is varied in the range of 0.25 ~ 7.5 % in volume. The MWCNTs grown at C_2H_2 concentrations between 1.5 ~ 3.5 % are well-aligned and are spin-capable. The well-aligned forests have higher areal density and shorter distances between the CNTs caused by strong Van der Waals interactions. CNTs grown at C_2H_2 concentrations under 1.5 % or over 3.5 % are curled and have random orientation. The resulting forests have reduced areal density and have poor spinnability. The thermal ramp rate is varied from 30 °C/min to 70 °C/min. Only the CNT forests grown with 50 °C/min condition are well-aligned and spinnable due to high areal density and closer spacing between adjacent CNTs. This condition alone results in Fe nanoparticles which have the proper size and density to produce spin-capable CNT forests.

Figure 1 shows SEM images and picture of spin-capable CNTs grown at 1.5 vol.% of acetylene and 50 °C/min on 70k Ω /sq Fe film at 780°C for 5min with mixture of He, H₂, and C₂H₂. The spinnable CNTs of 330 μ m have good alignment which is dependent on the ability to form ribbons. From a 1 \times 1 cm substrate, the CNTs can form a 4 m length sheet.

- [1] M. Zhang et al., *Science* **306**, 1358 (2004).
- [2] X. Zhang et al., *Adv. Mater.* **18**, 1505 (2006).
- [3] M. Zhang et al., *Science* **309**, 1215 (2005).
- [4] A. E. Aliev AE et al., *Science* **323**, 1575 (2009).
- [5] M. Zhang et al., *Science*, **306**, 1358 (2004).
- [6] X. Zhang et al., *Adv. Mater.*, **18**, 1505 (2006).
- [7] X. Zhang et al., *Small*, **3**, 244 (2007).
- [8] K. Liu et al., *Nano Lett.*, **8**, 700 (2008).
- [9] J-H. Kim et al., *Carbon*, **48**, 538 (2010).

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