

# Monday Morning, November 10, 2014

## Nanometer-scale Science and Technology

Room: 304 - Session NS+SE-MoM

### Delivering Energy and Mass at the Nanoscale

Moderator: Paul Sheehan, Naval Research Laboratory

8:20am NS+SE-MoM1 **Mechanical Properties of Polymer Systems Using Atomic Force Microscopy**, *Gregory Meyers*, The Dow Chemical Company **INVITED**

Scanned probe microscopy (SPM) has had a long history at The Dow Chemical Company, beginning in the late 1980s when commercial scanning tunneling microscopes were just hitting the market. Since that time Dow has invested in internal and external collaborative efforts to drive and develop atomic force based technologies for property measurements of polymeric materials at nanometer length scales.

Our most cited early work described a unique phenomenon of surface wear of polystyrene thin films where the interaction of a sliding AFM tip lead to characteristic patterns that depended on the polymer molecular weight. Since that time work such as this has been studied in order to understand elastic, adhesive, and thermal properties of polymer coatings and films near rigid interfaces. Collaborations with NIST in the late 1990s provided our first attempts at quantifying mechanical properties at the nanoscale, combining knowledge gained from classical nanoindentation to the calibration of AFM systems for quantitative AFM based indentation. This work set the stage for a large scale effort in the latter 2000 time frame, funded by the NIST-ATP program in collaboration with Veeco Instruments (now Bruker-Nano). The objective of this program was to develop an AFM based platform for quantitative modulus measurements of polymers at sub 100 nm length scales, to provide better than 10% precision for polymer materials with bulk properties in the 10 MPa to 10 GPa range. As a result of this program, we now have quasistatic AFM based indentation capability that provides the most comprehensive suite of analytical models (elastic, elastic-plastic, and adhesive) to interpret material properties at these scales. Within the last few years the ability to map properties at high spatial resolution via high speed AFM indenting has been realized. A key consideration in all of the mechanical probing is the time scale over which the tip-surface interaction occurs and so we have looked to computational simulations with Purdue University to study the role of dissipative factors – viscoelasticity and surface adhesion hysteresis – to help interpret our measurements.

9:00am NS+SE-MoM3 **Extension of Loss-Tangent Mode to Characterization of Materials' Stiffness and Damping**, *X. Yu, M. Tao, Nancy Burnham*, Worcester Polytechnic Institute

Viscoelastic materials are engineered and used in a variety of applications; however, it has been a great challenge to characterize their viscoelasticity at the nanoscale, at which the degradation and failure mechanisms often initiate. For linear viscoelastic materials, an atomic force microscopic (AFM) technique, loss-tangent mode, has been recently developed to fulfill this need [1]. The loss tangent of a material is expressed as the ratio of the lost energy (damping) over the stored energy (stiffness) and is claimed to be independent of the tip-sample contact area. Since this new mode was invented, only a few example materials have been studied. In this project, viscoelasticity of several different materials (i.e., asphalt binders [2], epoxy, silica tire, and graphite) were investigated using loss-tangent mode; the damping and stiffness terms were derived with easily measurable terms for a more detailed understanding of materials' viscoelasticity.

Results show that both free amplitude and set-point ratio affect the loss-tangent measurement. For all the examined materials, the loss tangent and damping decreased (power laws of  $-2.4 \pm 1.1$  and  $-2.1 \pm 1.0$ , respectively) with increasing free amplitude at constant set-point ratio, while stiffness increased (power law  $0.32 \pm 0.18$ ). The loss tangent increased (power law  $0.8 \pm 0.5$ ) with increasing set-point ratio at constant free amplitude; stiffness decreased more rapidly than damping (power laws of  $-1.75 \pm 0.06$  and  $-1.0 \pm 0.4$ , respectively). These trends might indicate that the loss tangent, as measured by AFM, is not independent of the tip-sample contact area. Computer simulation of loss-tangent mode is ongoing for explanation of these observations, in order to advance understanding of nanoscale viscoelastic measurements.

1. R. Proksch and D.G. Yablou, *Appl. Phys. Lett.* **100**, 073106 (2012)

2. X. Yu, N.A. Burnham, R.B. Mallick, M. Tao, *Fuel* **113**, 443 (2013)

9:40am NS+SE-MoM5 **Direct Mechanical Measurements of Viscoelasticity in Simple Liquids Using Vibrating Nanostructures**, *Matthew Pelton*, University of Maryland, Baltimore County, *D. Chakraborty*, University of Melbourne, Australia, *E. Malachosky, P. Guyot-Sionnest*, University of Chicago, *J.E. Sader*, University of Melbourne, Australia

Studies of acoustic vibrations in nanometer-scale particles can provide fundamental insights into the nanomechanical properties of nanoscale materials, and into the mechanical coupling between the nanoparticles and their environment. Metal nanoparticles allow for all-optical, non-contact measurements, using ultrafast laser pulses to generate and probe high-frequency acoustic vibrations. In early studies, the decay of the signal due to nanoparticle vibrations was dominated due to vibrations in nanoparticle size. By using highly uniform bipryamidal gold nanoparticles, we were able to overcome the effects of inhomogeneous damping and measure the rate at which the acoustic oscillations dissipate energy. Measurements in low-viscosity liquids such as water showed a strong "intrinsic" damping occurring within the nanoparticles themselves, and an environmental damping due to viscous coupling to the surrounding liquid. This fluid damping was described quantitatively using a parameter-free model.

In higher-viscosity liquids, however, the measured oscillation frequencies and damping rates deviate strongly and qualitatively from the predictions of this model. The deviations are explained quantitatively as arising from non-Newtonian effects in the liquid. The nanoparticles vibrate at very high frequencies (20 GHz), so that their vibration periods are comparable to the intrinsic relaxation times of the liquid. The structure-fluid interaction is thus dominated by viscoelastic effects. The observed viscoelasticity is not due to molecular confinement, but is a bulk continuum effect arising from the short time scale of vibration. This represents the first direct mechanical measurement of the intrinsic viscoelastic properties of simple bulk liquids, and opens a new paradigm for understanding extremely high frequency fluid mechanics, nanoscale sensing technologies, and biophysical processes.

10:00am NS+SE-MoM6 **Electronic and Optical Properties of Nanometer Sized Structures formed via Local Intercalated of Carbon in Layered Materials**, *Andrew Stollenwerk*, University of Northern Iowa

Electron beam radiation is often used to synthesize nanometer scale structures through lithographic techniques, direct altering of chemical bonds, or milling away material. We have recently demonstrated a new method to locally intercalate carbon with nanometer precision using the electron beam of a scanning electron microscope to break apart residual organics. This process was found to work only on layered materials such as topological insulators, novel superconductors, charge density wave materials, and graphite. Structurally, the incorporation of carbon raises the height of the substrate from a few nanometers up to several hundred nanometers depending on the exposure time. While easily observable using atomic force microscopy, these features are effectively invisible to the scanning tunneling microscope at tunneling biases below approximately 0.75 V. Tunneling spectrum of these structures exhibit semiconducting properties with band gaps varying between 0.5 eV – 2.5 eV. This is in agreement with the broad-wavelength photoluminescence observed in the corresponding optical spectrum. Both of these results suggest that the carbon intercalates form nano-clusters with a wide distribution in the size and density.

10:40am NS+SE-MoM8 **Effects of Chemical Bonding on Heat Transfer Across Interfaces**, *Paul Braun, M. Losego, M. Grady, N. Sottos, D.G. Cahill*, University of Illinois at Urbana-Champaign **INVITED**

Interfaces often dictate heat flow in micro- and nanostructured systems. However, despite the growing importance of thermal management in micro- and nanoscale devices, a unified understanding of the atomic-scale structural features contributing to interfacial heat transport does not exist. Herein, we experimentally demonstrate a link between interfacial bonding character and thermal conductance at the atomic level. Our experimental system consists of a gold film transfer-printed to a self-assembled monolayer (SAM) with systematically varied termination chemistries. Using a combination of ultrafast pump-probe techniques (time-domain thermoreflectance, TDTR, and picosecond acoustics) and laser spallation experiments, we independently measure and correlate changes in bonding strength and heat flow at the gold-SAM interface. For example, we experimentally demonstrate that varying the density of covalent bonds within this single bonding layer modulates both interfacial stiffness and interfacial thermal conductance. We believe that this experimental system will enable future quantification of other interfacial phenomena and will be a critical tool to stimulate and validate new theories describing the mechanisms of interfacial heat transport. Ultimately, these findings will

impact applications, including thermoelectric energy harvesting, microelectronics cooling, and spatial targeting for hyperthermal therapeutics.

11:20am **NS+SE-MoM10 Enhanced Thermal Transport at Covalently Functionalized Carbon Nanotube Array Interfaces to Oxide-forming and Noble Metals**, *S. Kaur*, Lawrence Berkeley National Laboratory, *N. Raravikar*, Intel Corporation, *B.A. Helms*, Lawrence Berkeley National Laboratory, *R. Prasher*, Sheetak, Inc., *D.Frank Ogletree*, Lawrence Berkeley National Laboratory

It has been more than a decade since the experimental demonstration that the thermal conductivity of carbon nanotubes can exceed that of diamond, which has the highest thermal conductivity among naturally existing materials. In spite of tremendous promise as a thermal material, results have been disappointing for practical thermal systems and applications based on nanotubes. The main culprit for the dramatic shortfall in the performance of nanotubes in practical systems is high thermal interface resistance between them and other components due to weak adhesion at the interface. We demonstrated a six-fold reduction in the thermal interface resistance between both oxide-forming and noble metal surfaces and vertically aligned multi-wall carbon nanotube arrays after bridging the interface with short, covalently-bonded organic molecules. Increased thermal transport was associated with a significant increase in interface mechanical adhesion [1]. Functionalized CNT thermal interfaces were shown to be stable in air for many months and resistant to thermal stress up to 180° C. We were also able to independently determine the intrinsic CNT interface resistance and the fraction of the CNT array contributing to thermal transport by performing multi-frequency time-domain thermo-reflectance (TDTR) measurements. Since our interface-functionalization method avoids destructive solution-phase processing, this development may lead to the practical integration of CNT arrays for thermal management in microelectronic devices

[1] "Enhanced thermal transport at covalently functionalized carbon nanotube array interfaces", Sumanjeet Kaur, Nachiket Raravikar, Brett A. Helms, Ravi Prasher & D. Frank Ogletree, *Nature Communications* 5 3082 (2014) doi: 10.1038/ncomms4082

11:40am **NS+SE-MoM11 Desktop Nanofabrication with Cantilever-Free Scanning Probes**, *Keith A. Brown*, *D.J. Eichelsdoerfer*, *X. Liao*, *C.A. Mirkin*, Northwestern University

The availability of reliable nanofabrication methods has dictated the pace of progress in many areas of physics, materials science, electronics, and biotechnology. A major deficiency in these fields is our inability to simultaneously control the architecture of soft materials from macroscopic to nanoscopic length scales. Scanning probe instruments, such as the atomic force microscope, are promising platforms for nanofabrication because they provide direct access to the nanoscale. However, the central barrier to their widespread use as lithographic instruments is throughput, as it is prohibitively slow to pattern large areas with a single nanoscale probe. To address this challenge, we explored a new architecture that utilizes a thin elastomeric film on a glass slide in lieu of cantilevers to enable the use of a massive array of probes in a simple format. Unfortunately, these cantilever-free probe arrays are passive duplication tools where each probe writes a copy of the same pattern. Here, we report on our recent advances in developing techniques for actuating individual probes in cantilever-free arrays and discuss the new scientific directions that these advances enable. Specifically, we present methods for both physically actuating cantilever-free probes using local heating and optically addressing probes that function as light valves for near-field photolithography, and find both to be capable of stitching together high resolution patterns that span multiple probes. These advances in nanofabrication have enabled new types of experiments, and in particular, we present recent progress in the combinatorial study of biochemical interactions and the high throughput fabrication of functional metamaterials using cantilever-free techniques. Taken together, these observations indicate that versatile desktop nanofabrication is possible using scanning probes and that these techniques can address the emerging challenges related to patterning soft materials.

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