

# Monday Afternoon, October 31, 2005

## Nanometer-Scale Science and Technology Room 204 - Session NS1-MoA

### Nanotribology

**Moderator:** H.J. Mamin, IBM Research Division

#### 2:00pm NS1-MoA1 Scaling Effects in Tribology: Micro- and Macroscale Studies of Diamond Like Carbon Nanocomposite Coatings, R.R. Chromik, North Carolina State University; K.J. Wahl, Naval Research Laboratory

The formation of a transfer film is a key part of how solid lubricant and protective coatings provide low friction and resist wear. These interfacial films, or "third bodies," are found to be chemically and mechanically different from the original mating surfaces, and the evolution of contact behavior is tied intimately with their dynamic nature. While the role of transfer films in macroscopic contacts has received considerable study, the effects of scaling on friction, transfer film formation and dynamics remains largely uninvestigated. To this end, we have studied the microtribology of DLC nanocomposite coatings using a commercially available nanoindentation system. Reciprocating sliding tests at speeds of 1-4  $\mu\text{m/s}$  were conducted using diamond and sapphire counterfaces having radii of 10 and 150  $\mu\text{m}$ , respectively. These geometries resulted in two regimes of contact stresses: 0.25 to 0.85 GPa for sapphire and 1.5 to 5.5 GPa for diamond. The friction behavior as a function of contact stress was explored in the elastic regime. Microcontact friction behavior fit a Hertzian contact model over a broad load range. Diamond vs. DLC gave shear stress similar to macroscopic values, while sapphire vs. DLC showed lower interfacial shear strength but higher friction overall. Ex situ optical microscopy, atomic force microscopy and micro-Raman spectroscopy suggest that friction response is correlated with formation of transfer films on the counterface. Scharf and I.L. Singer, Tribology Letters 14, 3 (2003). Ex situ optical microscopy, atomic force microscopy and micro-Raman spectroscopy suggest that friction response is correlated with formation of transfer films on the counterface. Singer, S.D. Dvorak, K.J. Wahl and T.W. Scharf, J. Vac. Sci. Technol. A21, S232 (2003).

#### 2:20pm NS1-MoA2 The Effect of Filling Carbon Nanotubes on Their Tribological Behavior, S.-J. Heo, S.B. Sinnott, University of Florida

As microengineering technology continues to evolve, the design of MicroElectroMechanical System (MEMS) / NanoElectroMechanical System (NEMS) devices is increasingly more complicated. At the same time, the need to consider the tribological properties of the materials that are likely components in future MEMS/NEMS devices has increased. Carbon nanotubes are one of the candidate materials for use in NEMS due to their high stiffness in the direction of the nanotube axis, low Young's modulus perpendicular to the nanotube axis and relative ease with which they slide against one another in bundles as a result of their van der Waals interaction with each other. In addition, nanotubes can stand high compressive and tensile forces prior to failure due to their flexibility. Here we investigate the responses of a bundle of single-walled nanotubes (SWNTs) and filled SWNTs to compressive and shear forces between two hydrogen-terminated sliding diamond surfaces by using classical molecular dynamics simulations. After constructing the systems, they are allowed to equilibrate completely at the room temperature. Then, the topmost diamond substrate moves to compress the nanotubes and then slides relative to the lower diamond surface in order to shear the nanotube bundle. The forces on the atoms are calculated by using the reactive empirical bond-order (REBO) potential for hydrocarbons coupled to Lennard-Jones Potentials. The results elucidate the role of filling on the tribological responses of SWNT bundles. This work is supported by the NSF-funded Network for Computational Nanotechnology (grant no. EEC-02288390).

#### 2:40pm NS1-MoA3 Nanometer Scale Mechanical and Electronic Properties of Molecular Films, M. Salmeron, Lawrence Berkeley National Laboratory

**INVITED**

Molecular thin films are intensely studied in connection with applications in chemical recognition, molecular patterning and manipulation, molecular electronics and as tribological films to modify friction and adhesion in nano- and micro-scale devices. I will present studies aimed at understanding the relation between structure, mechanical stability and electronic properties of molecular films. Our studies reveal the strong interdependence between structure and properties and the role of externally applied pressure. Examples include Self-assembled and Langmuir-Blodgett films made of molecules with saturated alkane chains, aromatic and unsaturated bonds, oligothiophenes, etc.

#### 3:20pm NS1-MoA5 On the Influence of Structure on Friction: The Amorphous-Crystalline Transition in Antimony Nanoparticles, C. Ritter, Humboldt University Berlin, Germany; M. Heyde, Fritz-Haber Institute of the Max-Planck Society, Germany; K. Rademann, Humboldt University Berlin, Germany; U.D. Schwarz, Yale University

This work addresses two of the crucial points in nanotribology, namely the dependence of friction on effective contact area and interface structure. As model system, antimony nanoparticles grown on graphite are used. Such particles can be easily prepared with different sizes, and the effective particle/substrate contact area can be deduced from scanning force microscopy images. Moreover, the particles are undergoing a structural transition from amorphous to polycrystalline during the growth process at about 10000-15000 nm in size. This feature can be used to establish a correlation between structure and friction. Antimony islands have been pushed over atomically flat substrate areas using the tip of a dynamic force microscope while the power dissipation necessary to move the islands was measured. To fully cover the amorphous-crystalline transition, to check on reproducibility, and to obtain sufficient statistics, 95 measurements including 57 islands (areas between 1370 nm<sup>2</sup> and 112000 nm<sup>2</sup>) and four different cantilevers were performed. The threshold value of the power dissipation needed for translation of the crystalline islands depends linearly on the contact area between the islands and the substrate. With the assumption of a linear relationship between dissipated power and frictional forces, this implies a direct proportionality between friction and contact area. The amorphous islands, however, also fit with a linear law, but the slope is a factor of three lower than the one found for the larger particles, leading to significantly lower energy dissipation. This change and their tentative relation to the structural transition within the particles will be discussed.

#### 3:40pm NS1-MoA6 Combined Nanoindenter and Quartz Microbalance Studies of Realistic Tribological Contacts and Ultrathin Lubricant Films, B. Borovsky, A. Booth, Grinnell College

For emerging technologies such as micromachined devices, it is increasingly important to understand high-speed, multi-asperity, microscale contacts lubricated with films as thin as a single molecule, and to control the effects of humidity. Most theoretical and experimental studies of small contacts do not directly access this physical regime. We have therefore used a combined nanoindenter and quartz crystal microbalance (QCM) to study the contact between a sapphire sphere and a polycrystalline gold electrode undergoing transverse shear at speeds on the order of 1 m/s. For the first time, we have used this combined system to study both dry and lubricated contacts, by applying monolayer octadecanethiol films. We have extended previous work by adding continuous monitoring of the QCM resonance bandwidth during indentations. We find that both the frequency and bandwidth of the QCM track changes in the contact area, as derived from the contact stiffness. Depending on the roughness of the gold electrode, variations in the frequency with contact area follow either the single-asperity or multi-asperity limits of the elastic no-slip model of the interface. However, this model fails to account for the large levels of dissipation observed during indentations and the dependence of the bandwidth on contact area. We attribute this to dissipation in outer portions of the contact subject to interfacial slip. We also report a reversible humidity effect whereby the levels of dissipation in lubricated contacts increase and decrease reproducibly with the amount of water incorporated into the octadecanethiol film. We will discuss refinements of the interaction model to account for frictional processes and the response of the polymer film to humidity, confinement, and high-frequency shear. Research supported by NSF, Research Corporation, and Hysitron, Inc. J. Wahl, J. Appl. Phys. 90, 6391 (2001).

#### 4:00pm NS1-MoA7 Effect of Temperature on the Nanomechanics of Lipid Bilayers Studied by Force Spectroscopy, S. Garcia-Manyes, G. Oncins, F. Sanz, University of Barcelona, Spain

The effect of temperature on the nanomechanical response of supported lipid bilayers has been studied topographically and by Force Spectroscopy with Atomic Force Microscopy. An AFM equipped with a high temperature stage heater has been used. It has been experimentally proved that the force needed to puncture a phosphatidylcholine lipid bilayer (yield threshold force,  $F_y$ ) deposited on mica and tested in liquid environment is extremely temperature-dependent. The quantitative measurement of the evolution of  $F_y$  with temperature has been related to the structural changes (phase transitions) that the bilayer undergoes as observed through AFM images. These studies have been carried out with three different

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phosphatidylcholine bilayers that exhibit different main phase transition temperatures (TM), namely, 1,2-Dimyristoyl-sn-glycero-3-phosphocholine(DMPC), 1,2-Dipalmitoyl-sn-glycero-3-Phosphocholine (DPPC) and 2-Dilauroyl-sn-glycero-3-Phosphocholine (DLPC). The solid-like phase shows a much higher  $F_y$  than the liquid-like phase, which also has been proved to exhibit a jump (breakthrough) in the force-curve. Within the solid-like phase  $F_y$  decreases as temperature is increased, and suddenly drops as it approaches TM. Interestingly, a well in the  $F_y$  vs. temperature plot occurs around TM, thus proving an anomalous mechanical softening around TM. Such mechanical softening has been predicted by experimental techniques and also by MD simulations and interpreted in terms of water ordering around the phospholipid headgroups. A further temperature increase when the phospholipid bilayer is in the liquid phase does not change  $F_y$  significantly. Furthermore, ion-binding has been demonstrated to increase  $F_y$  and its influence on both solid and liquid phases has also been discussed. @FootnoteText@ @footnote 1@Garcia-Manyes,S.; Oncins,G.; Sanz,F.:(Submitted to Biophysical Journal).

4:20pm **NS1-MoA8 Understanding the Frictional Response of Organic Monolayer Coatings using Atomic Force Microscopy, E.E. Flater, R.W. Carpick, University of Wisconsin-Madison**

Motivated by the lack of fundamental understanding of friction, and that friction and wear are major limiting factors for surface micromachined devices, we use atomic force microscopy (AFM) to determine the nanoscale frictional properties of alkylsilane monolayers commonly used in these microscale devices to reduce adhesion and friction. Quantitative single asperity measurements of friction and contact stiffness are performed using SiO<sub>2</sub>- and monolayer-terminated AFM tips on monolayer-terminated silicon. Using octadecyltrichlorosilane (OTS) and fluorinated monolayers (FOTAS), we observe that friction for these systems depends on the type of molecule and its packing properties. For the OTS monolayer there are two phases evident; the liquid condensed phase shows measurably lower friction at low loads than the liquid expanded phase, demonstrating that lower friction is associated with higher molecular packing density. However, the films exhibit the same frictional response at higher loads, indicating that compressed forms of both phases are tribologically equivalent. For FOTAS monolayer interfaces, fluorination increases friction at most loads, in agreement with measurements of micromachined interfaces. We find that frictional variation, as well as overall friction and adhesion for monolayer-coated tips are significantly reduced as compared with uncoated tips. Thus, the behavior of uncoated tips is highly dependent on the scanning history. This has wider importance for the acquisition of reproducible AFM nanotribology measurements in general, and strongly suggests that AFM researchers should strive to characterize and control the chemistry and structure of their tips to obtain meaningful measurements. We acknowledge Robert Ashurst for preparing the OTS samples, and Maarten de Boer and Alex Corwin for providing the FOTAS samples and microscale friction coefficients.

4:40pm **NS1-MoA9 The Observation of Nanoscale Melting at Sliding Interface, S.M. Lee, J. Krim, North Carolina State University**

Tribological phenomena occurring at buried interfaces undergoing shear are extremely difficult to characterize experimentally, especially since the characterizations must ideally be performed at both atomic length and time scales. We report here one such investigation, involving a scanning probe tip sliding along the metal film electrode of a quartz crystal microbalance (QCM). The atomically sharp STM tip allows the generation of the nano-scale interface area while the sharp resonance of QCM allows measurement of the interaction forces applied to its surface. This in turn yields fundamental information on energy dissipation mechanisms associated with the sliding. For a W-tip sliding along a copper surface, we have observed nano-scale melting that is attributable to the rubbing action of the tip. As the rubbing velocity at the interface increases, the frequency shift converted from the positive to the negative when the interface area melts. Additionally, QCM amplitude shifts are enhanced by ~ 5 times upon melting of the interface. This observation implies that the nano-scale local temperature can be controlled by the rubbing velocity at the film-tip interface. And the temperature rise by rubbing can easily go over 1000°C, since the melting point of copper is 1084.62°C. The experimental results will be discussed with in the context of an extended Laschitsch and Johannsmann (LJ) model.@footnote 1@ @FootnoteText@ @footnote 1@ B. Borovsky, J. Krim, S. A. Syed Asif, and K. J. Wahl, J. Appl. Phys., 90, 6391 (2001)@footnote \*@ This work has been supported by the DOE and the AFOSR Extreme Friction MURI program.

5:00pm **NS1-MoA10 Quantitative Elastic and Electromechanical Imaging: The Probe Dynamics of Vector Piezoresponse Force Microscopy, S. Jesse, A.P. Baddorf, S.V. Kalinin, Oak Ridge National Laboratory**

Piezoresponse Force Microscopy (PFM) is a nanoscale probe of the local coupling of electronic and mechanical properties, including domain imaging, polarization switching, hysteresis measurement, and orientation imaging of ferroelectric and piezoelectric materials. The image formation mechanism in PFM is controlled by the voltage dependent mechanics of the tip surface junction and the dynamics of the cantilever. A detailed analysis of the nanoscale tip-surface junction electromechanics junction shows that, for a conductive tip, the PFM signal is independent of tip shape, as in case for Atomic Force Acoustic Microscopy (AFAM). We analyze the frequency and DC bias dependent dynamic response of vector PFM, in particular, the transmission of vertical, lateral, and longitudinal surface vibrations to the tip, using modeling and 2D frequency-bias spectroscopy. We demonstrate that for an electrical tip excitation, the contact resonances are determined solely by the elastic properties of the material. Therefore, the tracking of contact resonance frequency permits local mechanical characterization, absent the numerous stray resonances inherent to piezo-actuators used in AFAM. The frequency dispersion of the nulling bias, the DC bias at which the measured response to AC excitation is zero, yields a measurement of electrostatic vs. electromechanical contrast. The differences between transduction for vertical and in-plane response components are analyzed. It is shown that lateral PFM imaging is optimal at low frequencies, while vertical PFM is best at high frequencies where dynamic stiffening reduces the electrostatic and longitudinal contributions. Finally, we discuss the measurements of all three components of the electromechanical response vector using a single PFM scan. Implications for molecular orientation imaging are also discussed. Research was performed as a Eugene P. Wigner Fellow (SVK) at ORNL, managed by UT-Battelle, LLC under DOE contract DCE-AC05-00OR22725.

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