Nanometer-scale Science and Technology
Room 2016 - Session NS+SS+TF-WeM

Nanotribology and Nanomechanics

Moderator: J. Harrison, U.S. Naval Academy

8:00am **NS+SS+TF-WeM1 Nanotribological Properties of Diamond-Like Carbon Thin Films: The Effect of Annealing on Nanoscale Adhesion and Friction**, ***D.S. Grierson***, *A.R. Konicek, A.V. Sumant, K. Sridharan, R.W. Carpick,* UW-Madison

Developing micro- and nano-scale devices with contacting or sliding parts continues to be challenging due to the poor tribological performance of conventional materials at the micro/nanoscale. The surface-to-volume ratio at small scales is high, and therefore materials with low nanoscale adhesion, friction and wear are needed to reduce tribological failures. Additionally, in applications where materials are subjected to cyclic thermal loadings, such as nanoscale thermomechanical data storage, the structure and tribological properties must remain stable. Diamond-like carbon (DLC) thin films have exceptional physical, chemical and tribological properties at the macroscale and are promising candidates for tribologically robust micro/nanoscale devices. We have studied the surface chemistry and nanotribology of undoped, Si-containing, and F-containing DLC, and investigated how annealing these films at 300°C in air affects these properties. We used the XANES (x-ray absorption near-edge spectroscopy), a surface-sensitive probe of the core-hole perturbed local density of unoccupied states, to understand the evolution of the surface chemistry and bonding. The sp@super 3@/sp@super 2@ ratio is increased by the addition of Si but not by F. The Si-containing DLC shows increased thermal stability. Atomic force microscopy (AFM) with DLC-coated AFM tips was used to conduct self-mated nanotribology experiments. The AFM results indicate that all DLC films exhibit adhesion on the order of van der Waals forces (~0.03 J/m@super 2@), and the nanoscale adhesion and friction on the Si-containing DLC are not affected by the thermal annealing. This indicates that DLC films, particularly those doped with Si, are highly promising for nanoscale thermomechanical device applications.

8:20am **NS+SS+TF-WeM2 Spectromicroscopy of Tribochemistry: X-PEEM Characterization of Wear vs. Humidity for Ultrahard Carbon Films**, ***A.R. Konicek***, *D.S. Grierson, A.V. Sumant,* UW-Madison*; N.N. Naguib, O. Auciello, J.A. Carlisle,* Argonne National Lab*; T.A. Friedmann, J.P. Sullivan,* Sandia National Labs*; J. Birrell,* Advanced Diamond Tech.*; P.U.P.A. De Stasio, R.W. Carpick,* UW-Madison

The outstanding tribological performance of carbon-based films can be seriously affected by variations in humidity. To explore the tribochemical origins of this behavior, self-mated interfaces of tetrahedral amorphous carbon (ta-C) and ultrananocrystalline diamond (UNCD) films were subjected to fretting wear in dry N2 with relative humidity values of 0%, 25% and 50%. Relative friction was measured during fretting, and the resulting wear tracks were examined with atomic force microscopy (AFM) and X-PEEM-XANES (X-ray PhotoElectron Emission Microscopy combined with X-ray Absorption Near-Edge Structure) spectromicroscopy. X-PEEM is capable of discerning chemical and bonding contrast at high spatial resolution, readily distinguishing between the wear track and the unworn film. For both films, friction increases as the relative humidity decreases. However, there are opposing trends in the behavior of graphitization and oxidation due to wear. For ta-C, as the relative humidity is decreased there is an increase in both graphitization and oxidation. This implies that the harsher wear environment has more heavily modified the carbon bonds compared to the wear at a higher relative humidity, inducing graphitization and oxidation. In contrast, the self-mated UNCD interface showed a comparative decrease in graphitization and oxidation in the wear track as the relative humidity was decreased. We will discuss changes observed in both friction and the chemical signature of the surface as the amount of relative humidity in the environment is varied. We will also discuss the relation between the amount of relative humidity in the environment and the level of graphitization that occurs in the wear track. @FootnoteText@ This work was partially supported by the US Department of Energy, BES-Materials Sciences, under Contract W-13-109-ENG-38.

8:40am **NS+SS+TF-WeM3 The Role of Atomic Corrugation, Crystal Orientation, and Surface Chemical Bonding in the Nanotribology of Carbon-Based Systems**, ***R.W. Carpick***, University of Wisconsin-Madison **INVITED**

A key challenge for nanotechnology lies in developing an understanding of nanotribology, particularly for materials with outstanding tribo-mechanical properties such as carbon-based films. Frictional slip and wear in these materials can be manifested in unique and surprising ways. As a fundamental example, we show that nanoscale friction can exhibit clear transitions from smooth sliding to single slips and then multiple slips. The slips are directly correlated with the atomic lattice of the sample, in this case pure graphite. The observation of the transition to multiple slips is new, and is understood by considering the competition between the stiffness of the interatomic interfacial potential and the elastic stiffnesses of the contacting materials and the force sensor itself. The transition to smooth sliding with ultralow dissipation in open air is observed for the first time, and atomic-scale stick-slip is observed for interfaces orders of magnitude larger than any previously tested. Atomic-scale stick-slip may therefore be a far more prevalent phenomenon than currently appreciated. We have also extensively studied the nanotribological behavior of other carbon-based systems, including single crystal and nanocrystalline diamond. The atomic structure of the surface, verified by detailed surface spectroscopy, critically affects friction and adhesion. Hydrogen termination is particularly effective in reducing friction and adhesion to the limit of van der Waals' interactions. Friction and adhesion are also affected by the crystal orientation. For larger tips, continuum mechanics models of contact area can be applied to understand the interfacial mechanics of these nano-scale contacts, as evidenced by the observation of direct proportionality between friction and contact area, a phenomenon known as "interfacial friction". By using smaller tips coated with a carbonaceous film, the limits of continuum mechanics are explored and discussed.

9:20am **NS+SS+TF-WeM5 Influence of the Solvent Environment on the Contact Mechanics of Tip-Sample Interactions in Friction Force Microscopy of Self Assembled Monolayers**, ***T.J. Colburn***, *G.J. Leggett,* University of Sheffield, UK

The application of friction force microscopy (FFM) to the characterisation of surface composition and nanoscale tribological phenomena requires an adequate understanding of the tip-sample contact mechanics. We present new data that show that the properties of the liquid medium influence not only the strength of the frictional interaction in FFM, but also the nature of the contact mechanics model that describes the tip-sample interaction. FFM measurements have been carried out on self assembled monolayers of dodecanethiol (C@sub 10@CH3) and mercaptoundecanoic acid (C@sub 10@COOH) in a variety of liquid media using tips functionalised with alkanethiols (chemical force microscopy). In perfluorodecalin, a liquid with a low dielectric constant, the friction-load relationship fits the behaviour predicted using the Johnson-Kendall-Roberts model for like pairs of interacting molecules, and the Derajuin-Muller-Toporov model for unlike molecules. In contrast, measurements in ethanol, a liquid with a larger dielectric constant, obey Amontons' law (i.e. the friction force is linearly proportional to the load). These findings suggest that single asperity contact mechanics are observed in media with low dielectric constants, where dispersion forces are very strong and frictional interactions are adhesion-controlled. In media with large dielectric constants, sliding is not adhesion-controlled and linear friction-load behaviour is observed.

9:40am **NS+SS+TF-WeM6 Indentation of Individual and Multiple Multi-Walled Carbon Nanotubes with AFM**, ***H.W. Yap***, *R.W. Carpick,* University of Wisconsin-Madison

There has been a recent surge of theoretical interest in the axial compression of MWCNTs, but only a limited number of experimental studies have been conducted. The study of axial compression of MWCNTs sheds light on their mechanical properties and has interesting implications in the fabrication of CNT - based composites. Lakes et al.@footnote 1@ have shown that macroscopic tubes have better damping properties in the post kink - buckled, snap-through regime, which is marked by a force drop with increased compression. Waters et al.@footnote 2@ and Qi et al.@footnote 3@ have indented an array of vertically aligned MWCNTs but have not observed force drops indicating these snap-through instabilities. Here, a stiff AFM cantilever with a microsphere tip attached to it is used to indent and compress a film of vertically-aligned MWCNTs with aspect ratio of ~35. These CNTs are grown with dc plasma-enhanced hot filament chemical vapor deposition from an anodized alumina nanopore template.

This is the first use of spherical probe AFM to compress aligned CNTs, though this method has been widely used in indenting biological and polymeric materials. Continuous cycles of loading and unloading to large strains were performed, and both large drops and finer relaxations in the loading portions of the force curves of a collection of MWCNTs were observed with a high degree of reproducibility. The drops are likely signatures of collective kink buckling instabilities seen in individual CNTs. The deformations, while nonlinear, are mostly elastic and reversible, as demonstrated by SEM images of the spherical tip and the sample after many cycles of deformation. We will discuss the implications of these results in the design of composites that take advantage of buckling instabilities for high damping applications. @FootnoteText@ @footnote1@Lakes et al.,Phil.Mag.Lett.,81,95(2001). @footnote2@Waters et al.,Appl.Phys.Lett.,85,1787(2004) @footnote3@Qi et al.,J.Phys.Mech.Sol.,51,2213(2003).

10:40am **NS+SS+TF-WeM9 Measurements and Modeling of Shear Modulus of Multiwalled Tungsten Disulfide Nanotubes**, *I. Kaplan-Ashiri,* ***S.R. Cohen,*** *N. Apter, H.D. Wagner, R. Tenne,* Weizmann Institute of Science, Israel*; G. Seifert,* Technische Universitat Dresden, Germany*; R. Shneck, D. Barlam,* Ben Gurion University, Israel

Recent investigations of the mechanical properties of inorganic fullerene have highlighted their unique properties.@footnote 1@ Although the bending modulus has been measured on single nanotubes, the shear modulus is much smaller and technically more difficult to ascertain. The S-W-S sandwich structure of individual layers of these inorganic nanotubes distinguish them chemically and mechanically from carbon nanotubes. The spacing of 6.18Å between layers is comprised of the tungsten disulfide entity, and a van der Waals gap. Direct measurements of the shear modulus of single tubes could elucidate how the tube mechanics are influenced both by the gap, and the interaction between the adjacent dichalcogenide atomic layers. Measurements were made in a scanning probe microscope (SPM) using a method similar to that described by Wu et al.:@footnote 2@ Nanotubes were dispersed on a grid structure consisting of trenches of depth 200 nm and width 500 nm. Scanning electron microscopy (SEM) was used to locate nanotubes which were appropriately aligned, and suspended over such a trench. These nanotubes were then glued to the substrate at the trench edge with amorphous carbon.@footnote 3@ The SPM was subsequently used to bend the suspended nanotubes from the side with the SPM probe by amounts ranging between 5 and 100 nm, while recording the lateral force. The results were analyzed by applying the bending equation using the known value of the bending modulus to extract shear modes. Results were further compared with both density functional calculations, and finite element analysis modeling, providing insights into mechanical interactions between the layers. @FootnoteText@ @footnote 1@ I. Kaplan-Ashiri, et al, Proc. Nat. Acad. Sci. 103, 523 (2006).@footnote 2@ B. Wu, et al, Nature Mat. 4, 525 (2005).@footnote 3@ Yu et al, Science 287, 147 (2000).

11:00am **NS+SS+TF-WeM10 Deformation Behavior of Low-Density Nanoporous Dielectrics**, ***S.O. Kucheyev,*** *P.M. Bythrow, T.F. Baumann, C.A. Cox, Y.M. Wang, T. van Buuren, A.V. Hamza,* Lawrence Livermore National Laboratory*; J.E. Bradby,* The Australian National University

Understanding deformation behavior of nanoporous glasses has recently regained tremendous interest in the community, primarily due to its importance for the development of a new generation of low-k dielectrics. Aerogels are sol-gel-derived nanoporous dielectric materials formed by nanometer size particles randomly interconnected into a solid network with a large degree of porosity and very high surface area. For these materials, the density can be varied from the theoretical maximum density (of a full density solid) to extreme cases of very high porosities (~99 %). Thus, aerogels represent a very attractive model system for studying the deformation mechanisms in nanoporous dielectrics. In this presentation, we discuss the use a combination of sound velocity measurements and nanoindentation with large spherical indenters (1-2 mm diameter) to study the deformation behavior of alumina and tantala aerogels with porosities up to 99%. In particular, we focus on how the deformation behavior is affected by (i) the average density of monoliths, (ii) the morphology and connectivity of nanoligaments, and (iii) the crystallographic phase. Results show that all of the above parameters can strongly affect the mechanical properties of nanoporous solids. Based on our results, we discuss the underlying deformation mechanisms and demonstrate an effective way to control mechanical properties of the nanoporous solids that can be synthesized with ligaments having a quasi-two-dimensional shape, such as platelets, ribbons, or leaflets. Work at LLNL was performed under the auspices of the U.S. DOE by the University of California, LLNL under Contract No. W-7405-Eng-48.

11:20am **NS+SS+TF-WeM11 Nanoporous Au - a 3D Network of Ultra-High Strength Nanowires**, ***J. Biener,*** *A.M. Hodge, J.R. Hayes, M. Duchaineau, L.A. Zepeda-Ruiz, A.V. Hamza, F. Abraham,* Lawrence Livermore National Laboratory

Recent mechanical studies on nanoporous gold (np-Au) have revealed that the yield strength of this material is almost one order of magnitude higher than predicted by scaling equations developed for open-cell foams. The higher-than-expected yield strength seems to be linked to the nanoscale morphology of np-Au which can be best described as a three-dimensional network of ultra-high strength Au nanowires. Here, we compare experimental results with molecular dynamics simulations to elucidate the nature of the high yield strength of nanoporous gold. This work was performed under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under contract of No.W-7405-Eng-48.

11:40am **NS+SS+TF-WeM12 Superconductivity Dependent Friction of Water, Nitrogen and Superheated He Films Adsorbed on Pb(111)**, ***J. Krim,*** *M. Highland,* North Carolina State University

The ability to predict sliding friction in adsorbed film systems underlies a vast range of topics in physics and nanotechnology, spanning the origins of static friction to the design of atomic-scale automobiles. One still hotly debated topic in this area is the degree to which electronic effects contribute to friction. In order to explore this issue, we have performed a quartz crystal microbalance study of sliding friction levels in nitrogen, water and superheated helium films adsorbed on Pb(111)@footnote 1@ and also self-affine fractal Pb substrates alternating in and out of the superconducting state. Reductions in friction upon entry into the superconducting state are greater for nitrogen than helium, consistent with a recent theory that linked electronic friction to adsorbate polarizability. Repetitive cycling of the externally applied magnetic field is observed to reduce overall friction levels.@footnote 2@ @FootnoteText@ @footnote 1@ M. Highland and J. Krim, Phys. Rev. Lett., in press (2006)@footnote 2@ Work supported by NSF and AFOSR.

12:00pm **NS+SS+TF-WeM13 In Situ Quantitative TEM Nanoindentation of Individual Nanoparticles and Nanoscale Materials**, ***Z. Shan,*** *A.M. Minor,* Lawrence Berkeley National Laboratory*; S.A. Syed Asif, O.L. Warren,* Hysitron Inc.

Monitoring the microstructure evolution while simultaneously measuring the stress and strain information at the nanometer level has been a long standing goal for material scientists. Here we show that by incorporating a miniature capacitive transducer into a TEM holder the load-displacement response (force resolution better than 0.5 ÂµN and displacement resolution better than 1 nm) can be achieved inside a TEM during the in situ nanoindentation process. A wide range of materials have been examined using this technique, such as Al thin films, single crystal Ni and Cu, Au and Cd metallic nanoparticles, and hollow shell-structured nanoparticles. The preliminary results will be reported and the physical insight derived from these results will be discussed. In particular, our results demonstrate unique insight into the initial deformation processes during the nanoindentation of metals and the analysis of elastic moduli and plasticity in nanoparticles.

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