Nanometer-scale Science and Technology Division
Room 612 - Session NS1-MoA

Nanoscale Tribology and Adhesion

Moderator: S.S. Perry, University of Houston

2:00pm **NS1-MoA1 Tribological Properties of Self-Assembled Monolayers on Si Surfaces***, **J.E. Houston**, J.D. Kiely,* Sandia National Laboratories*; J.A. Mulder, X.-Y. Zhu,* University of Minnesota

The use of organic monolayers as lubricating films has recently received considerable attention, especially with regard to their potential use in micromachine applications. We have used the interfacial force microscope (IFM) to characterize, on the nanometer scale, the tribological properties of a new class of self-assembled monolayers on Si(001) surfaces. These films consist of alkyl-OH and NH2 terminated molecules reacted with a fully chlorinated Si surface. We contrast their tribological behavior with those of the more familiar alkylchlorosilane monolayers through measurements of contact hysteresis, lateral frictional force and film conductance as a function of normal load. In addition, we probe the wear behavior under repetitive "wear-track" cycles. The chlorosilane monolayers show high friction coefficients and considerable wear while the films grown on the chlorinated surface show low friction coefficients and little wear, suggesting that the latter has considerable potential as a monolayer lubricant for Si. We discuss these results in terms of what is known concerning the structural and chemical properties of these two types of self-assembled monolayers. This work was supported by the U.S. Department of Energy under contract DE-AC04-94AL85000. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed-Martin Company, for the U.S. Department of Energy.

2:20pm **NS1-MoA2 Contact Hysteresis, Friction and Conductance of Self-Assembled Monolayers on Au***, **J.D. Kiely**, J.E. Houston,* Sandia National Laboratories

We have investigated the relationship between friction and the mechanical, electrical and chemical properties of self-assembled monolayers of hexadecanethiol on the Au(111) surface using the interfacial force microscope. We find a very low friction coefficient for freshly prepared films with a direct correlation of the frictional force with the contact hysteresis, i.e., the energy dissipated in the film during a loading/unloading cycle. In addition, the film conductance is found to increase exponentially with the applied film stress under loading. Above film stresses of about 4 Gpa, the film compliance and frictional force rise sharply while the conductance remains log linear. To simulate aging in a laboratory environment, we have oxidized films by direct exposure to ozone and find that the frictional force, conductance and hysteresis all rise dramatically. We discuss these results in terms of the known properties of the monolayer films and the findings of previous work on the effects of oxidation by ozone exposure. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

2:40pm **NS1-MoA3 Energy Dissipation in Defective Alkanethiol Monolayers***, **N.D. Shinn**, J.D. Kiely, J.E. Houston,* Sandia National Laboratories

Although highly ordered, alkanethiol self assembled monolayers (SAMs) have a hierarchy of structural defects that lead to dynamic energy dissipation.@footnote 1@ Counter-intuitive friction results on nominally isomorphic monolayers suggest surprising sensitivity to subtle structural differences or demonstrate that extrinsic probe/monolayer interactions dominate friction.@footnote 2@ We separate intrinsic and extrinsic contributions to friction by using a Quartz Crystal Microbalance to inertially shear and simultaneously measure the intrinsic energy dissipation in pure, mixed and damaged alkanethiol SAMs chemisorbed on Au(111)-textured QCM electrodes. For complete monolayers, domain boundaries are the major symmetry-breaking defects that enable dissipation. Point defects created by electron or UV irradiation only incrementally increase the intrinsic dissipation. Residual fluid phases, most notably in sub-monolayer films, lead to the highest dissipative losses. Oxidation by ozone decouples the SAM from the Au(111) substrate and dramatically increases the intrinsic dissipation. Interfacial Force Microscope experiments demonstrate how the structure-dependent SAM viscoelasticity is manifested in controlled friction measurements.@footnote 3@ Research supported by DOE-BES Materials Sciences. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000. @FootnoteText@@footnote 1@N. D. Shinn, T. M. Mayer and T. A. Michalske, Tribology Letts. (in press). @footnote 2@ H. I. Kim, T. Koini, T. R. Lee and S. S. Perry, Langmuir 13, 7192 (1997). @footnote 3@J. E. Kiely, N. D. Shinn and J. E. Houston, Langmuir (submitted).

3:00pm **NS1-MoA4 Interaction Forces Measured with Functionalized Cantilevers and SFM Modulation Techniques***, **A.L. Szuchmacher**, R. Luginbuehl, T. Engel, R.M. Overney,* University of Washington

Understanding local interaction forces between material surfaces is very important for many industrial and research applications such as tribology, materials science, bioengineering, and polymer science. The scanning force microscope allows for measuring forces acting at those interfaces. In order to understand the interactions between probe and material surfaces, the surface chemistry of the SFM tip must be well defined. Ultrasharp silicon cantilevers were reacted with different silanes to produce well defined and covalently bound monolayer films. The quality of these coatings was controlled by different techniques including ESCA and SFM. These tips were used to study the interactions of thin films using force-displacement curves and friction force measurements. Special SFM modulation techniques were applied to probe and image the interfacial interactions. Amplitude and phase response signals will be discussed. Fundamental effects of solvents on van der Waals interactions between surfaces were investigated as well as hydrogen bonding effects. Experiments were carried out as a function of surface chemistry, temperature, solvent, and pH.

3:20pm **NS1-MoA5 SPM Tip-Sample Interactions in Primary Alcohols of Varying Chain Length***, **R.M. Ralich**, Y. Wu, R.D. Ramsier, P.N. Henriksen,* University of Akron

Interactions between functionalized tips and substrates in scanning probe microscopy (SPM) are usually investigated by utilizing an intervening liquid medium, however the results may be influenced in various ways by the medium itself. In this study the chain length of a series of primary alcohols is shown to affect adhesion measurements. The measurements are performed between a layer of phosphonic acid adsorbed on an aluminum substrate and an aluminum-coated, hydroxyl-terminated silicon nitride tip. These are adsorption systems that have been characterized previously by vibrational spectroscopy and form a stable, well-defined system for studying the effects of the medium on adhesion. Adhesion forces between the tip and sample are observed to decrease as the alcohol chain length is increased. These data imply that a synergistic combination of fundamental interactions is responsible for adhesion in this system.

3:40pm **NS1-MoA6 Sliding Friction of Xenon Monolayers and Bilayers on Pb and Cu Substrates***, **S.M. Winder**, B. Mason, J. Krim,* North Carolina State University

Studies of the fundamental origins of friction have undergone rapid progress in recent years with the development of new experimental and computational techniques for measuring and simulating friction at atomic length and time scales.@footnote 1@ The increased interest has sparked a variety of discussions and debates concerning the nature of the atomic-scale mechanisms that dominate the dissipative process by which mechanical energy is transformed into heat. We report here our measurements of the sliding friction of xenon monolayers and bilayers sliding on Cu and Pb surfaces. Such studies provide information on the relative contributions of electronic and phononic dissipative contributions to sliding friction, since phonon dissipation is present at all film coverages, while electronic dissipation primarily impacts the monolayer. For the system Xe/Pb the relative contributions of monolayer and bilayer coverages to the measured friction appear similar to those of Xe/Ag(111).@footnote 2@ This indicates the primary mechanism of friction in Xe/Pb and Xe/Ag is through phonons within the adsorbate. The substrate Pb is of particular interest on account of the recent observation of superconductivity-dependent sliding friction on this metal. The system Xe/Cu is interesting because the interaction potential of Xe/Cu is known accurately, allowing highly reliable comparisons of theory to experiment. Work funded by NSF DMR#9896280. @FootnoteText@ @footnote 1@ J. Krim, Scientific American, vol. 275, pp 74-80 (1996). @footnote 2@ C. Daly and J. Krim, Physical Review Letters, vol. 76, pp 803-806 (1996).

4:00pm **NS1-MoA7 Tribological Proprties of Single Crystalline Metal Surface***, **A.J. Gellman**, J.S. Ko,* Carnegie Mellon University **INVITED**

The tribological properties of single crystal metal surfaces have been measured under the ultra-high vacuum conditions of a surface analysis apparatus. This experiment allows us to measure both friction and adhesion between two single crystal surfaces brought into contact under a wide range of loads, and sheared with a wide range of sliding velocities. Most importantly it is possible to maintain strict control over the chemistry and properties of the surfaces. The experiments performed to date have systematically varied a number of surface characteristics in order to observed their effects on tribological properties. The clean surfaces of singles crystals can be brought together under varying orientation. Experiments with Ni(100) surfaces have shown that the crystallographic orientation can affect the frictional properties of the interface. These result in variations of the friction coefficients over a fivefold range. Furthermore the effects of crystallographic oreintation propagate through adsorbed layer of thickness up to four monolayers. The effects of orientation are thought to result from plastic deformation in the bulk solid of the metal crystals. The effects of adsorbed species can be measured with an extremely high level of control over the nature of the adsorbate, its coverage and its chemistry. On both Cu(111) and Ni(100) surfaces we have observed that at coverages less than one monolayer adsorbed species have little or no influence on interfacial friction. This has been observed using both atomic and molecular adorbates. It is thought that for adsorbed films at coverages less than one monolayer direct metal-metal junctions across the interface cause displacement of adsorbed species from the contact region. The result is a metal-metal interface with high shear strength similar to that formed between clean surfaces. Finally, the friction between single crystal surfaces can be influenced by fine characteristics of the structure of adsorbed layers. Measurements reveal discontinuous breaks in the friction versus adsorbate coverage for both trifluoroethanol on the Cu(111) surface and ethanol on the Ni(100) surface. These discontinuities are attributed to layering of the adsorbate on the surface. The observation of such effects has been made in several laboratories using the surface forces apparatus to measure friction between perfectly flat mica surfaces. It is remarkable to see similar effects occuring between crystalline metallic surfaces that are plastically deformable.

4:40pm **NS1-MoA9 Combined Quartz Crystal Microbalance and Scanning Probe Microscope Studies of Vapor-Deposited Films on Metal Surfaces*, B. Borovsky*, *M. Abdelmaksoud, J. Krim,* North Carolina State University

Experimental investigations of friction, lubrication and adhesion at nanometer lengthscales have traditionally been performed by employing force microscopy, surface forces apparatus (SFA), or quartz crystal microbalance (QCM) techniques. While collectively these techniques have yielded much useful information, their results have to date never been mutually cross-referenced. In order to achieve such a cross referencing, we have performed two sets of measurements: (1) A QCM study of the system toluene/Ag(111) with and without C@sub 60@ vapor-deposited on the Ag(111) surface, and (2) a joint QCM/SPM study of the systems Ethylene/Pt and Oxygen/Ag. The former system has been studied by means of SFA,@footnote 1@ whereby it was reported that C@sub 60@ at a toluene/mica surface resulted in a significant reduction in friction levels. The latter studies allow direct comparison of SPM and QCM data, as the measurements are carried out in unison. Our studies of toluene/C@sub 60@ have revealed that the decrease in friction reported in Ref. 1 is most likely due to the manner in which the C@sub 60@ layer adheres to the solid substrate. Meanwhile, we have observed that for ethylene and oxygen adsorbed on Ag, a measurable shift in the frequency and amplitude response of the QCM occurs as the STM tip is dragged through the adsorbed layers. Additionally, allowing rubbing to proceed for extended periods within a small scanned region produces a large contrast with the surrounding region in STM images. The experiment is currently being repeated on a Pt substrate in order to search for a tribochemically-triggered reaction. Work funded by AFOSR F49620-98-1-02-1 and NSF DMR9896280 @FootnoteText@ @footnote 1@ S.E. Campbell, G. Luengo, V.I. Srdanov, F. Wudl and J.I. Israelachvili, Nature, volume 82, p 520 (1996) .

5:00pm **NS1-MoA10 Sliding Transitions and Dissipation in Nanoscale Contacts*, K.J. Wahl,*** Naval Research Laboratory*; S.A.S. Asif,* University of Florida

In order to investigate tribological processes at the nanometer scale, we need to better understand how model asperity contacts respond to shear and dissipate energy. In our experiments, we investigate the dynamic processes occurring during the transition from static to sliding contact, as well as during the formation and breaking of nanoscale adhesive contacts. Measurements are made using an atomic force microscope operated in shear modulation mode, where the sample position is modulated laterally with amplitudes as small as a few Å. Both amplitude and phase response of the contacts are monitored using a lock-in amplifier. In this work, we expand our technique to incorporate harmonic analysis of the response of the contact to lateral modulation. As a result, we are now able to distinguish between various types of dissipation including friction, microslip and damping. We demonstrate application of this technique to discriminate between static to sliding contacts as well as identify and quantify microslip in nanoscale contacts.

Author Index

Bold page numbers indicate presenter