Monday Morning, November 2, 1998

Nanometer-scale Science and Technology Division Room 321/322/323 - Session NS+SS-MoM

Tribology, Adhesion and Interfacial Forces Moderator: J.E. Houston, Sandia National Laboratories

8:20am NS+SS-MoM1 Nanotribological Interactions: Hard and Soft Interfacial Junctions, *U. Landman*, Georgia Institute of Technology INVITED Certain aspects of the dependence of materials properties on their size will be addressed, particularly at the nanometer length scale where new behaviour emerges when the physical dimensions of the system approach, or are reduced below, a characteristic length relevant for the phenomenon or physical process being probed. We focus on computer simulation studies of formation mechanisms, structural, mechanical, electronic, transport, dynamic and rheological properties of nanoscale hard (solid nanowires) and soft (confined liquid) interfacial junctions. These issues are central to research in nanotribology, that is explorations of the atomic and molecular scale origins and methods of control of friction and lubrication, and are relevant to modern miniaturization technologies. Work supported by DOE and AFOSR.

9:00am NS+SS-MoM3 Measuring Nanocontact Adhesion and Deformation, J.B. Pethica, University of Oxford, United Kingdom INVITED Nanoscale probe techniques such as nanoindentation and AFM have given new insight into contact mechanics, and hence into adhesion and tribology problems. Almost all local mechanical, and several electrical parameters of the component surface materials can be measured. The key is a reliable determination of the test probe displacement (lateral as well as normal) as a function of applied forces. Accurate determination of storage and loss moduli in thin polymer films, along with their frequency and temperature variation, will be described as one example of these capabilities, and of the associated stringent experimental requirements. During the approach to contact, sensitive force-distance spectroscopy, close to atomic scale spatial resolution, allows mapping of the interaction potential between the surfaces. Some of the outstanding problems will also be discussed. These include the effect of adsorbates, especially on the onset of irreversible or dissipative deformation, and the determination of contact area in systems which are anything other than clean and homogeneous.

9:40am NS+SS-MoM5 Adhesive Interactions and Damage Mechanisms in Scanning Probe Microscopy: A Study by Interfacial Force Microscopy, *J.F.*

Graham, O.L. Warren, P.R. Norton, University of Western Ontario, Canada It is often observed that contact mode scanning probe imaging with hard tips at loads of 10's of nN will damage soft surfaces, such as those of polymers. We have studied the origin of damage mechanisms on cellulose acetate (CA) calibration grids with the interfacial force microscope (IFM) using parabolic tungsten probes of 100 to 200 nm radius and forces of ~ 75 nN. The parabolic geometry of our W tips possesses a smooth profile at the apex with no sharp or discontinuous edges that can cause exceedingly high and damaging local stresses. The CA grid (elastic modulus ~ 2 GPa) can be imaged many times with a clean tungsten tip (modulus ~370 GPa) without visible damage, provided the maximum static force does not exceed that for plastic deformation of the CA. This force is readily and quantitatively determined by the IFM. After determination of a force (f) versus distance (d) curve (from which the nanomechanical properties are derived) during which the plastic limit of the CA was exceeded, contact mode imaging at the same force which had previously caused no damage, produced rapid, irreversible damage to the CA surface. It was also observed that there was a distinctive adhesion event (in the sense that it was not related to capillary forces) in the withdrawal curves of those f-d curves which preceeded damage. Further, occasionally we observed a sub-micron polymer particle on the surface after operation of the IFM in the tapping mode after an indentation experiment. This specific adhesive interaction (as well as the capillary forces) was eliminated by carrying out the measurements under hexadecane. The origin of the damage mechansim therefore appears to be: 1. the adhesive transfer of polymer to the tip; 2. the formation of adhesive contacts between this polymer "coated" tip and the CA surface; 3. repetitive formation and breaking through shear forces of polymerpolymer contacts at the interface.

10:00am NS+SS-MoM6 Friction and Adhesion in the Attractive Regime, A.R. Burns, J.E. Houston, R.W. Carpick, Sandia National Laboratories

Recent molecular level measurements and simulations have shown a strong connection between adhesive bonding forces and energy dissipation

in sliding friction. In order to observe this directly, we have constructed a scanning force microscope with de-coupled lateral and normal force sensors to simultaneously observe the onset of both friction and chemical bond formation. Furthermore, by using a mechanically-stable interfacial force sensor,@footnote 1@ we are able to map the entire attractive interaction between the probe tip and the sample surface. Measurements made on self-assembling alkanethiol films with chemically different head groups show that friction can be directly attributed to bond formation and rupture well before repulsive contact. Thus we are able to separate chemical friction from more traditional mechanical sources of energy dissipation.@footnote 2@ @FootnoteText@ @footnote 1@ S. A. Joyce and J. E. Houston, Rev. Sci. Instrum. 62, 710 (1991). @footnote 2@ 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.

10:20am NS+SS-MoM7 Tribology and Mechanical Properties of Langmuir-Blodgett Monolayers, K.J. Wahl, W.R. Barger, S. Asif, Naval Research Laboratory

Mechanical properties of contacts with nanometer-scale dimensions are important in understanding the behavior of microscale sliding contacts. Monolayer films provide a model system to study fundamentals of relationships between adhesion, friction and mechanics. In this study, we deposited monolayers of distearoyl phosphatidyl ethanolamine (DSPE) and dioleoyl phosphatidyl ethanolamine (DOPE) (both mixed and single component) on freshly cleaved mica by the Langmuir-Blodgett technique. We use atomic force microscopy to examine morphology, adhesion and shear (sliding) behavior as well as modulation techniques to investigate mechanical properties of the monolayers as a function of deposition pressure. Measurements of film elastic/viscoelastic mechanical response via force modulation techniques are compared and contrasted with the surface compressional modulus determined during film deposition as well as to mechanical properties via nanoindentation.

10:40am NS+SS-MOM8 Deformation and Friction of Organic Monolayers, J.D. Kiely, J.E. Houston, Sandia National Laboratories

The use of organic monolayers as lubricating films has received considerable attention recently, especially with regard to their potential use in micromachine applications. We have used the interfacial force microscope (IFM) to characterize, on the nanometer scale, tribological properties of alkanethiol self-assembled monolayers on Au and monolayers of octadecyltrichlorosilane and perfluorodecyltrichlorosilane on Si. The IFM is similar to the atomic force microscope (AFM) but is distinguished by it use of a quantitative, mechanically stable, zero-compliance force sensor which allows us to measure both normal and frictional forces in a controlled fashion (i.e., without 'snap-to-contact'). We quantitatively relate monolayer deformation (chracterized by using the IFM in a nanoindentation mode) to friction, and find that, in the absence of appreciable adhesion/adhesion hysteresis, friction is very well correlated with deformation hysteresis. Additionally, we have identified the effects of wear, monolayer preparation procedure, and the environment (e.g., UV exposure and humidity) on tribological properties. This work was supported by the U.S. Department of Energy under Contract DEAC04-94AL85000. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed-Martin Company, for the U.S. Department of Energy.

11:00am NS+SS-MoM9 Structure-Dependent Viscoelasticity During Alkane Thiol Monolayer Growth, N.D. Shinn, T.M. Mayer, T.A. Michalske, Sandia National Laboratories

Organic monolayers adsorbed on contacting surfaces (e.g., as micromachine lubricants) modify both the chemistry and the mechanical properties of the interface. Whereas the chemistry can be predicted from the terminal functionality of the individual molecules, the viscoelastic properties reflect inadequately understood molecular ensemble dynamics. For example, the isomorphic self-assembled monolayers of methylterminated alkane thiol homologues [HS(CH@sub 2@)@sub n-1@CH@sub 3@ denoted as C@sub n@] have complex shear moduli that vary by orders of magnitude. We are using Acoustic Wave Damping (AWD) techniques and spectroscopic ellipsometry to elucidate the structure-dependent viscoelasticity of alkane thiols on polycrystalline Au(111) quartz crystal microbalance substrates. Multi-frequency analysis yields the complex shear modulus of equilibrium structures and a high-sensitivity oscillator circuit @footnote 1@ permits simultaneous measurement of the adsorption kinetics and energy dissipation during monolayer growth from the gas phase. Monolayer elasticity increases with alkane chain length. Co-

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adsorbed physisorbed molecules, chemisorbed two-dimensional fluid phases, and the nucleation and growth of condensed-phase islands each contribute to dissipation in the growing monolayers. Short chain (n < 10) thiol monolayers grow via Langmuir kinetics into a two-dimensional gas phase followed by slow condensation into ordered domains. However, the C@sub 12@ thiol exhibits surprising precursor-mediated kinetics and a highly viscous initial phase. Thiol dimerization is considered as a mechanistic explanation for the observed differences. 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@@footnote1@ K. Wessendorf, Sandia Nat. Labs. (patent pending).

11:20am NS+SS-MoM10 Lubrication Brought to Light: Optical Signatures of Nanomechanical Effects in Organic Thin Films, *R.W. Carpick*, *D.Y. Sasaki, S. Singh, A.R. Burns*, Sandia National Laboratories

The properties of organic lubricant films composed of hydrocarbon chain molecules is currently of great interest, as the detailed molecular response of these films to mechanical stress remains to be understood. Molecular films of polydiacetylenes are composed of ordered hydrocarbon chains attached to a chromophoric polymer backbone. These materials exhibit strong fluorescence emission and optical absorption which can be altered by mechanical stress (mechanochromism), providing the opporutunity to exploit the optical response as a signature of specific molecular behavior. Furthermore, structurally distinct chromatic phases ("blue" and "red" phases) of the film can be produced by a combination of Langmuir-Blodgett deposition and photopolymerization. We have studied the response of these films to mechanical stress at the nanometer level using a novel scanning force microscope. The instrument combines near-field optical detection with a displacement-controlled (non-compliant) normal force sensor and a decoupled lateral force sensor. Nanomechanical properties, including local elastic modulus, adhesion, and friction are compared for different chromatic phases of the film. We examine the modes of film deformation at the molecular level by monitoring the fluorescence emission while varying the mechanical stress applied to a nanometer-sized contact area. * 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.

11:40am NS+SS-MOM11 In-situ Investigation of the Influence of a Mechanical Load on the Orientation of Organic Monolayers with Second Harmonic Generation, *M. Gurka*, *F. Eisert*, *M. Buck*, *M. Grunze*, University of Heidelberg, Germany

Understanding mechanical properties of ultrathin organic films is of fundamental importance due to their vital role in numerous technological applications such as hard disc drive lubrication or as moulde release agents in the injection moulding process. The relationship between macroscopically applied forces and processes taking place on the molecular scale can be studied in situ by photon-based techniques. Second harmonic generation (SHG) is a nonlinear optical technique which allows to investigate the effect of normal and shear forces on the order and orientation of confined monolayers. We have set up a model experiment consisting of an SHG-active silane film self-assembled onto a glas prism. A pressure in the range of 30 - 50 MPa is applied to the monolayer by pressing a quartz lens against the prism. Changes of the film structure are monitored by in situ polarization dependent SHG experiments. The SHG signal reflects the response of the SHG-active endgroup of the monolayer to the mechanical load and allows to determine the average tilt angle of the monolayer and also the in-plane symmetry of the molecular layer. During loading we observe only a minor change in the mean tilt angle of the endgroup whereas shear forces cause the molecules to align.

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