

# Monday Afternoon, November 3, 2003

## Surface Science

### Room 327 - Session SS2-MoA

#### Tribology, Adhesion, and Friction

**Moderator:** S.P. Jarvis, Trinity College Dublin, Ireland

2:00pm **SS2-MoA1 Super Hydrophobic Interactions: From the Inside and Out**, *J.E. Houston*, Sandia National Laboratories; *S. Singh*, University of New Mexico; *C.J. Brinker*, Sandia National Laboratories

Considerable interest has recently been directed toward the study of the processing of "super hydrophobic" (SH) surfaces and their unique properties. These materials are generally characterized by hydrophobic molecules in a fractal-like structure and have contact angle in excess of  $\sim 150^\circ$ . We present here studies of the behavior of the interaction force vs. relative separation between a scanning force-probe tip and sample surface using the interfacial force microscope (IFM). The measurements include "inside" interactions for both a SH film (contact angle  $\sim 165^\circ$ ) and hydrophilic tip ( $\sim 30^\circ$ ) coming into contact with the SH surface in water, and the "outside" case for a SH-coated tip in contact with the outer water surface. As expected, the latter case shows the development of a considerable repulsive force before becoming unstable submersing the coated-tip end. However, the inside case shows a marked contrast depending on the nature of the tip. The hydrophilic tip shows only repulsive forces, as it essentially pushes against the inside surface of the water in contact with the SH film. In addition, the SH surface deformation reveals an unusual creep behavior in this case. In contrast, the SH coated tip shows large, long-range attractive forces prior to contacting the SH film, an effect which is often characterized as due to interfacial bubble formation. These results will be discussed in terms of experimental parameters, such as tip speed and the thickness of the SH film, as well as the mechanical properties of the film itself, both wet and dry. The work at Sandia was supported by the DOE Office of Basic Energy Sciences, Division of Materials Sciences. Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin company, for the DOE under Contract DE-AC04-94AL85000.

2:20pm **SS2-MoA2 Friction Anisotropy at Pd(100)/Pd(100) Interfaces**, *A.J. Gellman*, *C.M. Mancinelli*, Carnegie Mellon University

Friction anisotropy has been studied between two Pd(100) single crystal surfaces in an ultrahigh vacuum environment. Friction measurements were made using Pd(100)/Pd(100) interfaces modified by adsorption of octane at coverages ranging from 4 to 40 molecular layers. The relative crystallographic orientation of the two Pd(100) surfaces was systematically varied and friction measurements were made at each orientation as a function of octane coverage. These measurements have revealed that friction is anisotropic with respect to Pd(100) lattice orientation. When the surfaces were aligned, forming a commensurate interface, and sheared along the direction with 4ML of octane at the interface, the static friction coefficient was  $\mu_{\text{static}} > 8.0 \pm 2.0$ . A minimum in the static friction coefficient was obtained when the two Pd(100) surfaces with 4ML of octane at the interface were misoriented by  $\theta \sim 45^\circ$ . Under these conditions the static friction coefficient for sliding along the direction of the stationary surface was  $\mu_{\text{static}} = 4.0 \pm 2.0$ . Higher coverages of octane decreased the friction, but friction anisotropy persisted for coverages of octane as high as 20 ML at the sliding interface between the two Pd(100) surfaces. Wear scars were observed on both surfaces indicating that plastic deformation had occurred during sliding. The observation of friction anisotropy in the presence of disordered overlayers of octane and during shearing of surfaces that deform plastically suggests that friction anisotropy originates with the properties of the bulk crystal lattices rather than surface lattice commensurability. These results corroborate the findings of a previous study of friction anisotropy between Ni(100) surfaces. @FootnoteText@ @Footnote 1@ Langmuir, 2000, 16(22), 8343.

2:40pm **SS2-MoA3 Direct Observation of Superlubricity**, *J.W.M. Frenken*, Leiden University, The Netherlands; *M. Dienwiebel*, IAVF AG, Germany; *N. Pradeep*, *K.B. Jinesh*, *G.S. Verhoeven*, Leiden University, The Netherlands; *J.A. Heimberg*, Corvis Corporation

We have constructed a frictional force microscope (FFM) that is able to quantitatively track the forces between a tip and sample in three dimensions. At the heart of the FFM is a silicon sensor, the 'Tribolover'. The 3D motion of a metal tip, which is held by this sensor, is detected with four interferometers. The two lateral spring constants of the Tribolovers are typically 1 N/m, which is up to two orders of magnitude lower than the

torsional force constants of conventional AFM cantilevers. The spring constant perpendicular to the surface is typically an order of magnitude higher than in the lateral directions. The friction force resolution is as low as 15 pN, even under normal loads up to several tens of nN. We present experiments with W-tips on highly oriented, pyrolytic graphite (HOPG) surfaces. We observe the familiar, atomic-scale stick-slip behavior, in which the tip performs a 'least-resistance', zig-zag path over the corrugated graphite surface. To our surprise, the amplitude of the friction forces depends strongly on the relative orientation of the tip and the graphite surface. When we rotate the graphite around an axis normal to the surface, the average friction force shows characteristic variations between a high value and a near-zero value, close to the detection limit of our FFM. These observations, combined with additional, circumstantial evidence, support a simple interpretation, in which a small graphite flake intervenes between the W tip and the HOPG substrate. Thus, the FFM actually records the lateral forces between two parallel graphite lattices. By rotating the substrate with respect to the tip, we periodically go through fully aligned and completely misoriented configurations. When the misalignment is sufficiently severe, the lateral forces on the C-atoms in the flake cancel, thereby dramatically reducing the total friction force. This phenomenon has been predicted more than ten years ago, and is referred to as superlubricity.

3:00pm **SS2-MoA4 The Role of the Third Body Processes in the Friction and Wear of MoS<sub>2</sub> and MoST Coatings**, *G.Y. Lee*, *I.L. Singer*, *K.J. Wahl*, U.S. Naval Research Laboratory

The sliding friction behavior of MoST@footnote 1@ (Ti-Mo-S) and MoS@sub 2@ coatings has been investigated by in situ tribometry, which allowed real time observation of third body dynamics. The coatings were deposited by closed field unbalanced magnetron sputtering and contained between 0 to 20 % titanium. Reciprocating tests were performed in both dry (< 4 % RH) and ambient (40-50 % RH) air at a sliding speed of 1 mm/s and 24 N normal load (1.1 GPa mean Hertzian stress) using sapphire hemispheres as counterbodies. All coatings showed similar steady-state friction coefficients: about 0.025 in dry air and 0.06 in ambient air, however titanium containing coatings in ambient air exhibited lower friction coefficients at the beginning of the tests. Titanium containing coatings also showed reduced wear in both dry and ambient conditions. In situ optical microscopy observations identified the formation of a transfer film (third body) on the sapphire hemisphere for all tests. Most of the sliding took place between the transfer film and the wear track indicating that the velocity accommodation was interfacial sliding. The titanium containing coatings exhibited an additional velocity accommodation mode, shearing and extrusion of transfer film, correlated to the higher friction in ambient conditions. The role of the transfer film mobility and mechanical properties in controlling friction behavior will be discussed. @FootnoteText@ @footnote 1@ N.M. Renevier, V.C. Fox, D.G. Teer, and J. Hampshire, Surf. Coat. Tech., 127 (2000) 24-27.

3:20pm **SS2-MoA5 Molecular and Bulk Material Mechanisms of Smooth and Stick-slip Sliding**, *J. Israelachvili*, University of California, Santa Barbara  
**INVITED**

There are at least three quite different contributions to the friction force between two ideal surfaces, i.e., smooth surfaces sliding in the absence of wear: load-dependent friction (which depends on the surface structure or topography), adhesion-dependent friction (which depends on any adhesion between the two surfaces) and viscosity-dependent friction (which occurs when the shearing surfaces are separated by a thin layer of liquid). These contributions depend on the surface molecular structure, the contact area, applied load (or pressure), film thickness, film viscosity, and sliding speed (or shear rate). In addition to these purely surface or interfacial properties, the bulk properties of the materials such as the elastic modulus can also play an important role even in the case of wearless sliding of elastic surfaces. Thus, depending on their shape, the friction can be smooth or proceed via stick-slip. The situation with rough and/or viscoelastic surfaces can be very rich and complex, as can the adhesion between the surfaces, and both may depend critically on a combination of surface and bulk properties. The talk will review some recent experimental results, including theoretical modeling and computer simulations, on such systems, i.e., both rough and smooth, hard and soft, adhesive and non-adhesive, lubricated and unlubricated. Such studies are clarifying the molecular basis of many well-established tribological laws and empirical observations such as Amontons laws and the Stribeck Curve, and are also revealing new insights and relationships between tribological processes at the molecular and macroscopic levels.

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4:00pm **SS2-MoA7 Evaluation of the Surface Characteristics and Mechanical Properties of Interconnect Films and their Correlation with CMP Process**, *P.B. Zantye, A.K. Sikder, A. Kumar*, University of South Florida  
Chemical Mechanical Planarization (CMP) has emerged as one of the most widely used Back End of Line (BEOL) semiconductor manufacturing process for fabrication of present generation Cu interconnect structures. CMP is synergistic combination of tribological and chemical phenomena occurring at the surface of the polishing pad and wafer in presence of chemically active slurry. Thus, the frictional forces that act upon the wafer during CMP assume significant importance for effective characterization of the CMP process. In this research the surface characteristics and mechanical properties of various candidate materials Cu (wiring metal) and interlayer dielectrics (ILD) SiLK@super TM@ (soft polymer), and SiO@sub2@ (ceramic) have been evaluated. The surface roughness of the candidate materials was determined using the Atomic Force Microscopy (AFM) technique. The mechanical properties (Young's Modulus and Hardness) of Cu, SiLK@super TM@ and SiO@sub2@ were evaluated using MTS Nanoindenter@superTM@. The material removal behavior and dry friction characteristics were studied by micro scratch testing and the CMP process of materials under investigation was simulated on the Bench Top CMP tester. The coefficient of friction (COF) was monitored in situ during initial and final part of wafer coupon polishing. The surface characteristics, mechanical properties, dry friction and material removal were then correlated with the CMP process for each material to get an insight in to the polishing behavior of these candidate materials when planarized with different material specific slurries and polishing pads.

4:20pm **SS2-MoA8 A Comparative Study of the Adhesion, Friction, and Mechanical Properties of CF@sub3@ and CH@sub 3@ Terminated Alkanethiol Monolayers**, *C.M. Doelling, H. Ying*, Princeton University; *J.E. Houston*, Sandia National Laboratories; *T.K. Vanderlick, G. Scoles*, Princeton University; *T.R. Lee*, University of Houston

Considerable interest has been given to the potential use of self-assembled monolayer films as lubricants for applications such as MEMS. Of particular interest are fluorinated films because they are inert and show high thermal stability. Research performed directly compares the adhesion, friction, mechanical properties and contact potentials of two alkanethiol SAM films, differing only in the composition of their terminal head group (-CH@sub 3@ vs. -CF@sub 3@). Quantitative data of both friction and normal force was collected using the Sandia-developed interfacial force microscope (IFM). In comparison with the CH@sub 3@-terminated monolayer, we find that the CF@sub 3@-terminated film exhibits a longer-ranged attraction to an approaching metal probe tip, and the work required to separate the surfaces is greater despite the maximum attractive forces being similar. The friction is also larger, as is the force-displacement hysteresis upon loading/unloading cycles. Close inspection of the frictional response shows the presence of "non-contact" friction, namely, significant energy dissipation before the probe and monolayer develop a component of repulsive-contact force. From these findings we conclude that the mechanical behavior of the film is influenced by the strong dipole inherent to the -CF@sub 3@ terminal group. Finally, atomic force microscopy measurements of friction were also undertaken, taking advantage of nanografting to directly compare both types of films using the same probe tip. At small compressive loads, the friction of the fluorinated film is about two times that of the hydrocarbon film, in agreement with the IFM results. @FootnoteText@ The work at Sandia was supported by the DOE Office of Basic Energy Sciences, Division of Materials Sciences. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin company, for the DOE under Contract DE-AC04-94AL85000.

4:40pm **SS2-MoA9 Reaction of Trimethylphosphate with TiC and VC(100) Surfaces**, *H.I. Kim, P. Frantz, S.V. Didziulis*, The Aerospace Corporation; *L.C. Fernandez-Torres, S.S. Perry*, University of Houston

Hard coatings, such as titanium carbide (TiC), are emerging technologies for various tribological applications, including spacecraft bearings due to their higher hardness and greater wear resistance compared to metal components. However, their surface chemical properties, especially with respect to high-performance lubricants, are poorly understood. Therefore, the adsorption and chemical reaction of a model lubricant additive, trimethylphosphate [(CH<sub>3</sub>O)<sub>3</sub>PO] (TMP), were investigated on the surfaces of TiC and VC(100) as a function of temperature using high-resolution electron energy loss spectroscopy (HREELS), X-ray photoelectron spectroscopy (XPS) and temperature programmed desorption (TPD). TMP adsorbs molecularly on both surfaces at cryogenic temperature, and chemical bonding to the surface is evident upon warming to approximately 200 K. At higher temperatures, surface chemical reaction on TiC leads to

phosphate-like and carbonaceous products that persist on the surface after heating up to 873 K. The stability of these surface species at such high temperature presents potential implications for modification and lubrication of hard coating surfaces at high temperatures where most organic adsorbates fail to provide tribological benefits. The reaction pathway and the reaction products are determined to be dependent on the initial coverage as well as the substrate chemistry, i.e. TiC vs. VC. These results have interesting implications for potential applications in boundary additives on hard coatings, where desired surface chemical protection may be tuned by the concentration of the organophosphate ester additives in the lubricant and the substrate chemistry.

5:00pm **SS2-MoA10 Degradation of Self-Assembled Monolayer in Humid Environments**, *B.-I. Kim, T.M. Mayer, M.G. Hankins, M.P. de Boer, B.C. Bunker*, Sandia National Laboratories

Self-assembled monolayers (SAMS) are used extensively to control friction and stiction in micromachines. While as-prepared coatings are effective at minimizing adhesion, coating performance can deteriorate with time in humid environments. We are using the interfacial force microscope (IFM) to monitor the aging behavior of SAMS as a function of temperature, humidity, time, SAM composition, and fabrication procedures. The IFM provides force-distance curves between functionalized scanning probe tips and substrate surfaces while avoiding the "snap-to-contact" problems associated with conventional atomic force microscopy (AFM). We have simultaneously measured both normal and friction forces between a tip and SAM coated surfaces as a function of separation distance. Together with topographic images taken with AFM, we can correlate adhesion and friction with structural information. Our results indicate that adsorbed water can disrupt hydrogen bonds at the SAM-substrate interface, reorganizing the coating to create bare patches that promote adhesion. To date, coatings that have been tested include standard octadecyl trichlorosilane (OTS), tridecafluoro-1,1,2,2-tetrahydrooctyltrichlorosilane (FOTS), octadecene (reacted with surface Si-H bonds), dichlorodimethylsilane (DDMS), and an octadecyl coupling agent attached to the surface using amine functional groups. At all humidities and temperatures tested, it appears that FOTS coating that have been annealed to promote condensation reactions with surface silanols are most effective at resisting degradation in hot, humid environments. @FootnoteText@ 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.

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