Thursday Morning, November 18, 2004

Surface Science
Room 210C - Session SS2-ThM
Tribology, Adhesion, and Friction

Moderator: I.L. Singer, Naval Research Laboratory

8:40am **SS2-ThM2 Advanced Adhesion Test Methods for Semiconductor Interconnect Film***, **A.K. Sikder**, N. Gitis, M. Vinogradov,* Center for Tribology, Inc.

For faster signal propagation in integrated circuits, new materials with lower dielectric constant (low-k) values are required with copper metal lines. Low-k materials possess many challenges due to their poor mechanical integrity and weak adhesion to other interconnects, so it is important to characterize their adhesion behavior. There are numerous techniques known for adhesion and delamination testing of coatings, some of the most common being a tape test, stud-pull test, scratch test and an indentation test. Each of them has its advantages, but neither one is universally effective for soft to hard, ultra-thin to thick films. The new testing technology, based on multiple sensors coupled with servo-control of forces and displacements, has been developed to fill this void. A novel technology for scratch testing has been developed in order to evaluate the tribo-mechanical behavior of interconnect thin films, where an indenter moves in both vertical (loading) and horizontal (sliding) directions, while acoustic emission and electrical resistance sensors allow for detection of the initiation of fracture, and the scratch pattern indicates the type of failure. The impression left by scratch testing is then observed using scanning probe and optical microscopy, integrated into the instrument mod. UNMT. Scratch testing on various interconnect blanket and patterned, single and multilayered, polished and unpolished film is presented. Adhesion and delamination characteristics are discussed with respect to the intrinsic properties of the different interconnect films (low-k, copper and tantalum) and their surface roughness. Their effective testing in the stack of the films is complimented by frictional and acoustic measurements. The multi-sensing technology allowed for comprehensive characterization of the scratch, adhesion and durability of thin coatings.

9:00am **SS2-ThM3 Light vs. Heavy Diamond: an Investigation of the Fundamental Origins of Friction***, **R.J. Cannara**, R.W. Carpick,* University of Wisconsin-Madison

Mechanisms of friction include wear, bond-breaking and surface chemistry, molecular deformation, electronic dissipation, and vibrational excitations (or phonons). Resolving the individual contribution of each of these mechanisms poses a great challenge. To overcome this obstacle and isolate the role of phonons in frictional energy dissipation, we compare insulating crystals that are identical, except for having different isotopic concentration. We report adhesion, as well as load- and temperature-dependent nano-scale friction measurements, for a tungsten carbide-coated Si tip on the hydrogen-terminated (111) surfaces of three single-crystal synthetic Type IIa diamonds. Each of the specimens is composed of a different bulk mixture of @super 12@C and @super 13@C. Varying the average mass and isotopic disorder in diamond strongly influences its phonon band structure and thermal properties. For example, previous work has revealed that both phonon lifetimes and thermal diffusivity of diamond increase with isotopic purification. Moreover, its thermal diffusivity is dramatically enhanced at low temperatures (down to ~100 K). All of these phonon properties determine the probability that atomic vibrations (initially created by slip processes during sliding) will reduce frictional energy dissipation by aiding subsequent slip events. We discuss isotope, or phonon, contributions to atomic-scale friction measurements performed in nitrogen and ultra-high vacuum at different temperatures. In addition, we present evidence for structural interfacial effects that lead to negative differential friction behavior.

9:40am **SS2-ThM5 Frictional Forces and Amontons' Law: From the Molecular to the Macroscopic Scale***, **U. Landman**, J. Gao, W.D. Luedtke,* Georgia Institute of Technology **INVITED**

Amontons' law, which was already known to Leonardo da Vinci, states that the friction force is directly proportional to the (normal) applied load, with a constant of proportionality - the friction coefficient - that is constant and independent of the contact area, the surface roughness and the sliding velocity. No theory has yet satisfacorily explained this surprisingly general law, all attempts being model or system dependent. On the basis of large-scale molecular dynamics simulations pertaining to lubricated adhesive and non-adhesive junctions, with morphologically rough (as well as crystallographically flat) confining solid surfaces, and in conjunction with recent experiments, we show that the local energy-dissipation mechanisms are not 'mechanical', as assumed in most models, but â?othermodynamicâ?□ in nature. We show that a local analysis of the simulation results, based on division of the system into small cells, leads to a natural description in terms of the Weibull distribution. For the dynamic. non-equilibrium, energy-dissipating process that we study, this long-tail distribution serves a similar purpose as the Boltzmann distribution for classical systems at equilibrium. While Amontons' law does not hold on the local scale, it is recovered on the global scale, with the spatio-temporal averaging utilizing the Weibull distribtion of the local friction forces. Interestingly, the concept of "area of contact", often used in frictional studies, does not enter into our analysis. J. Gao, W.D. Luedtke, D. Gourdon, M Ruths, J.N. Israelachvili, U. Landman, Feature Article, in J. Phys. Chem. B 108, 3480 (2004).

10:20am **SS2-ThM7 Activation of SiC Surface for Vapor Phase Lubrication by Chemical Vapor Deposition of Fe***, **D. Kim**, A.J. Gellman,* Carnegie Mellon University

Vapor phase lubrication (VPL) has been proposed as a method for lubricating high temperature engines. During VPL, lubricants such as tricresylphosphate (TCP), (CH@sub 3@-C@sub 6@H@sub 4@O)@sub 3@P=O, are delivered through the vapor phase to high temperature engine components where they react to deposit a thin, solid, lubricating film. Although ceramics such as SiC are desirable materials for high temperature applications their surfaces are unreactive for the decomposition of TCP and thus not amenable to vapor phase lubrication. As a means of activating the SiC surface for TCP decomposition we have used chemical vapor deposition of Fe from Fe(CO)@sub 5@. Modification the SiC surface by the presence of Fe accelerates subsequent decomposition of TCP and deposition of P and C on the surface. m-TCP decomposes more readily in the temperature range of 300 K - 500 K on Fe-coated SiC surfaces than on SiC surfaces. The C and P deposition rates depend on the thickness of the Fe film and are further enhanced by oxidation of the Fe. This work provides a proof-of-concept demonstration of the feasibility of using vapor phase to lubricate ceramics.

10:40am **SS2-ThM8 In Situ Studies of Interfacial Rheology of MoS2 and Most Solid Lubricating Coatings***, G.Y. Lee, I.L. Singer,* Naval Research Laboratory*; **K.J. Wahl**,* Naval Research Laboratory, US

Materials properties (e.g. composition, microstructure, and mechanics) of both solid lubricant coatings and their interfacial transfer films have long been recognized as important to tribological performance. These properties are generally evaluated ex situ, before and after sliding have occurred. However, in situ observations of contacts have shown that interfacial rheology - the deformation and flow of matter within the contact - plays a significant role in controlling friction, wear and endurance of solid lubricants. In this paper, we will present real-time observations of interfacial rheology of MoS2 and MoST@footnote 1@ (Ti-Mo-S) coatings using in situ tribometery. The coatings were deposited by closed field unbalanced magnetron sputtering and contained between 0 and 20% titanium. Reciprocating tests were performed in both dry (<1%) and ambient air (45-60% RH) at 1-4 mm/s and under 1.1 GPa mean contact stress. The interface rheology was studied quantitatively using optical microscopy techniques. Transfer film buildup and depletion were monitored quantitatively using interference fringes, while interfacial dynamics (locus of sliding, stability, and strain rate) were evaluated through video microscopy. The interfacial rheology of MoS2 coatings was strongly influenced by environment (dry vs. humid). In contrast, interfacial rheology of MoST coatings was far less sensitive to humidity, but was strongly influenced by evolution of wear track surface composition and morphology. We will demonstrate how these quantitative measures of interfacial rheology can be used to help us interpret how transfer films influence friction, wear and endurance of MoS2-based solid lubricant coatings. @FootnoteText@ @footnote 1@ D.G. Teer, Wear 251 (2001) 1068-1074.

11:00am **SS2-ThM9 Self-Assembled Monolayers: The Origin of Molecular Level Friction***, **R.C. Major**, X.-Y. Zhu,* University of Minnesota*; J.E. Houston,* Sandia National Laboratories

Functionalized self-assembled monolayers (SAMs) are being used in a broad spectrum of disciplines to control the chemical and physical properties of surfaces at the molecular level. Despite a large number of studies, current understanding of the mechanical properties of these functional SAMs is rather incomplete. This arises in part because of the difficulty in quantitatively measuring adhesion and friction forces on the molecular level, and due to the non-trivial task of preparing well-ordered, functionalized thiol monolayers containing reactive endgroups (e.g. HS-(CH@sub 2@)@sub n@-COOH vs HS-(CH@sub 2@)@sub n@-CH@sub 3@) on Au(111) substrates; the latter has often been overlooked in the past literature. Here we report a quantitative study on the tribological properties of functionalized SAMs on Au(111) using Interfacial Force Microscopy (IFM). We show the intimate relationship of tribological properties with the chemical state of the SAM. For example, in the case of -COOH terminated SAMs, we observed a dramatic reversible change in friction response corresponding to the protonated and deprotonated state of the -COOH groups. This frictional response showed an interesting dependence on the conformation and length of the alkyl chains. Microscopic models correlating chemical interactions to tribological properties at the interface will be discussed. This work was supported by Sandia National Laboratories a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin company, for the DOE under Contract DE-AC04-94AL85000.

11:20am **SS2-ThM10 Nanotribological Effects of Substrate Surface Order and Partial Fluorination for Alkanephosphonic Acid Self-Assembled Monolayers on Alumina***, **M.J. Brukman,*** University of Wisconsin-Madison*; T.D. Dunbar,* 3M Company*; R.W. Carpick,* University of Wisconsin-Madison

SAMs are of considerable interest for applications such as lubrication, corrosion protection, and water repellency, particularly at the nano-scale. Here, we compare the wettability and nano-scale friction and adhesion of two phosphonic acid self-assembled monolayers (SAMs): CF@sub 3@(CF@sub 2@)@sub 7@(CH@sub 2@)@sub 11@-PO@sub 3@H@sub 2@ (F8H11 PA) and CH@sub 3@(CH@sub 2@)@sub 17@-PO@sub 3@H@sub 2@ (H18 PA) deposited on a series of three Al@sub 2@O@sub 3@ surfaces: C- and R- plane single crystal sapphire, and an amorphous alumina layer on Si. Contact angle measurements were performed to compare the wetting of fluorinated and hydrogenated SAMs by water and hexadecane. Atomic force microscopy was then used to characterize the nano-scale dependences of adhesion and friction on SAM composition and substrate surface order. We observe differences that depend on the substrate, indicating that substrate-imposed variations in packing density and ordering have measurable nanotribological effects.

11:40am **SS2-ThM11 Tribological Behavior of Self-Assembled Double Layer Measured by a Pin-on-plate Method***, **M. Nakano**, T. Ishida, T. Numata, Y. Ando, S. Sasaki,* National Institute of Advanced Industrial Science and Technology, Japan

We investigated the tribological behavior of self-assembled double layers using pin-on-plate method in this study. Previously we have been investigated the tribological behavior of alkanethiol self-assembled monolayers using pin-on-plate method and X-ray photoelectron spectroscopy [1]. We found that the friction coefficient was dependent on the alkylchain length and that even a monolayer film has sufficient durability against friction, although the friction coefficients measured at 0.2-0.3 were slightly high. It was pointed out that formation of a new overlayer on monolayer could lead to decrease the friction. From this point of view, here we investigated the tribological behavior of self-assembled double layers using pin-on-plate method. Double layer preparation on Au substrates was performed in a glass beaker at room temperature. Substrates were first exposed to a 1 mM of mercaptohexadecanoic acid solution in ethanol for 24 h. Then, the samples were exposed to a 1 mM of copper acetate solution in ethanol for approximately 5 min. Finally, the samples were exposed to a 1 mM of octadecanethiol solution in ethanol for 24 h [2]. The frictional properties of the SAMs were examined by a pin-on-plate tribometer with a load of 30 mN and sliding speeds of 1 mm/sec (0.2 Hz). The friction coefficient on double layer was kept at 0.10-0.15 for about 30 min, indicating that the topmost octadecanethiol layer was expected to act as the mobile layer and effective to decrease the friction. Ref. [1] M. Nakano, T. Ishida, T. Numata, Y. Ando, S. Sasaki: Jpn. J. Appl. Phys. 42 (2003) 4735. [2] H. Ohno, L. A. Nagahara, W. Mizutani, J. Takagi, H. Tokumoto: Jpn. J. Appl. Phys. 38 (1999) 180.

Author Index

Bold page numbers indicate presenter