Tribology

Room: 617 - Session TR1+MN-WeA

Surfaces and Interfaces in MEMS

Moderator: J.A. Harrison, United States Naval Academy

1:40pm **TR1+MN-WeA1 Glassy-like Behavior of GaAs Nanomechanical Oscillators at Millikelvin Temperatures**, ***S.B. Shim***, *S.W. Cho,* Seoul National University, Korea*, N. Kim, J. Kim,* Korea Research Institute of Standards and Science*, Y.D. Park*, Seoul National University, Korea

We report on the mechanical properties of single crystalline GaAs doubly-clamped beam resonator structures characterized by magnetomotive techniques in millikelvin temperatures. Clean nanomechanical GaAs resonators are realized from a lattice-matched GaAs/InGaP/GaAs heterostructures without plasma etching processing with typical quality (Q) factor of ~ 17,400 at 45 mK with resonance frequency of 15.816 MHz. We find dissipation (Q^{-1}) to have weak temperature dependence ($\sim T^{0.32}$) as compared to Si nanomechanical resonators of similar size ($\sim T^{0.36}$).[1] Furthermore, we find shift in the resonance frequency as function of temperature to be nontrivial with a crossover behavior (i.e. at low temperatures shift in the resonance frequency is positive with increasing temperature and at high temperature (T > ~1 K), negative). Such observations are similar to those observed in sound attenuation experiments in disordered glass systems.[2] We will also discuss other possible dissipation mechanisms as well as the effect of differing surface conditions and treatments.

[1] G. Zolfagharkhani et al., PRB 72, (2005).

[2] W.A. Phillips, Rep. Prog. Phys. 50, 1657 (1987).

2:00pm **TR1+MN-WeA2 MEMS Tribology in Extreme Environments**[1], ***J. Krim***, North Carolina State Univ.*, M. Aggleton,* Univ. of California at Irvine, *C.J. Brown,* North Carolina State Univ.*, J.C. Burton,* Univ. of California at Irvine, *D.A. Hook,* North Carolina State Univ.*, J. Wenner,* Univ. of California at Irvine, *M.T. Dugger,* Sandia National Labs, *A. Morris,* WiSpry, Inc.*, J.E. Rutledge, P. Taborek*, Univ. of California at Irvine **INVITED**

Microelectromechanical systems, MEMS, have become a remarkably successful technology since the beginnings of MEMS development 30 to 40 years ago. However the overwhelming majority of MEMS are used near room temperature and atmospheric pressure. Consequently there is little empirical data to guide the design of MEMS for use in environments such as space where low pressures and cryogenic temperatures must be tolerated. In addition, it is well known that friction and wear severely constrain MEMS design. MEMS that have sliding contact between surfaces have shorter lifetimes and lower reliability than MEMS that do not. We have measured the characteristics of two microelectromechanical systems, namely a silicon sidewall tribometer and an RF MEMS direct contact switch, at cryogenic temperatures and in ambient gas environments below atmospheric pressure, and report on the tribological issues and possible solutions for operation of MEMS in such extreme environments.

[1] This work has been supported by EXTREME FRICTION AFOSR MURI #FA9550-04-1- 0381, and partially by Sandia National Laboratories. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DE- AC04-94AL85000.

2:40pm **TR1+MN-WeA4 Performance of RF MEMS Switch Contacts at Cryogenic Temperatures**, ***C.J. Brown***, *J. Krim,* North Carolina State University, *A.S. Morris III*, wiSpry, Inc.

A series of experiments were performed to characterize RF MEMS switch performance under variable pressure, atmospheric conditions and temperature. A vacuum system was constructed allowing for switch operation in cryogenic temperatures and pressures in the miliTorr range. Vacuum environments were chosen to limit stiction failures due to moisture; however the switches encountered bouncing problems at closure for low pressures. Helium and nitrogen were chosen as substitute atmospheres to lower stiction failure rates while circumventing switch bouncing issues. Contact resistance measurements were taken across a temperature range of 77 to 293 Kelvin using both gasses. Results showed no differences in contact resistance due to atmospheric conditions except at cryogenic temperatures. Contact resistance values were observed to be lower at cryogenic temperatures but are orders of magnitude higher than values predicted for constriction resistance in gold asperity contacts. Results obtained across the cryogenic temperature range support the conclusions of previously published work at high temperatures, which asserted changes in contact resistance were due mostly to the presence of thin films on the contacts.[1] Additionally, the data indicates these films are less mobile at cryogenic temperatures. Application of the asperity-heating model indicates contact voltages can applied which selectively disassociate films from the contact surface while not softening the gold asperity contacts. This research is funded by AFOSR MURI Grant No. FA9550-04-1-0381.

[1] B. Jensen, L. Chow, K. Huang, K. Saitou, J. Volakis and K. Kurabayashi, "Effect of nanoscale heating on electrical transport in RF MEMS switch contacts," J. Microelectromechanical Systems, vol. 14, no. 5, pp. 935-946, 2005.

3:00pm **TR1+MN-WeA5 Macro-, Micro-, and Nano-scale Lubrication using Alcohol Vapor: Implications to MEMS.**, *D.B. Asay,* Pennsylvania State University, *M.T. Dugger,* Sandia National Laboratories, ***S.H. Kim***, Pennsylvania State University

Friction, adhesion, and wear are dramatically affected by the environment in which surfaces come into contact. In the case of an alcohol vapor environment, the silicon surface reacts to form an alkoxide. Shearing these surfaces also produces higher weight oligomers. These molecules are continuously replenished in the contact region, drastically reducing wear and friction provided that the alcohol vapor pressure is near or above the vapor pressure required for monolayer coverage. At these conditions, the lubricating layer protects the silicon surfaces with little to no wear observed. Tribological properties are reported at the nanoscopic (AFM), mesoscopic (MEMS), and macroscopic (tribometer). In all cases, the vapor successfully lubricates and minimizes wear. In the case of MEMS sidewall friction, the lifetime of the device is radically increased.

4:00pm **TR1+MN-WeA8 MEMS Reliability in Harsh Environments**, ***R. Maboudian***, *C. Carraro*, University of California at Berkeley **INVITED**

Many applications require sensors and actuators that can survive harsh environments, including high temperature and high relative humidity. This presentation will examine the behavior of polycrystalline silicon based micro-electromechanical systems in a variety of harsh environments. Then, the effectiveness of self-assembled monolayers and silicon carbide for enhanced MEMS reliability under these conditions will be discussed.

4:40pm **TR1+MN-WeA10 Water Vapor Effects on the Lubrication of Silicon MEMS by Alcohol Vapor***,* ***M.T. Dugger***, Sandia National Laboratories, *D.B. Asay,* Pennsylvania State University*, J.A. Ohlhausen,* Sandia National Laboratories*, S.H. Kim*, Pennsylvania State University

Adhesion, friction and wear have been the greatest limitations to development of robust MicroElectromechanical Systems (MEMS) that rely on contact between surfaces. Chemisorbed monolayers such as alkyl and amino-silanes have been successful in creating initially-free structures, but have not demonstrated adequate long duration operation in sliding contacts, and recent studies suggest that they degrade with long term static exposure to water vapor in storage. A new lubrication approach has been demonstrated on silicon surfaces, which consists of alcohol molecules in the vapor phase that form a friction and wear reducing film dynamically, preferentially at contact locations. ToF-SIMS analysis of wear tracks from pin-on-disk experiments suggest formation of high molecular weight oligomers where the stress is highest. Experiments with MEMS tribometers result in a factor of at least 10^5 increase in operation life without failure, and no wear or debris formation. Practical device operation requires lubrication in the presence of some concentration of water vapor inside sealed packages. Friction experiments in environments containing 400 ppm alcohol and 1000 ppm H_2O show that lubrication by alcohol is inhibited at these relative concentrations.

[*] Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000.

5:00pm **TR1+MN-WeA11 Monolayer Degradation and Sidewall Tribometer Studies of Vapor Phase Lubricants for MEMS**, ***D.A. Hook***, Sandia National Laboratiories, North Carolina State University, *S.J. Timpe,* Sandia National Laboratiories, University of California Berkeley, *M.T. Dugger,* Sandia National Laboratories*, J. Krim*, North Carolina State University

Long hydrocarbon and fluorocarbon-based monolayers have been widely used in MEMS applications to prevent release related stiction as well as adhesion as devices are stored for long periods of time.[1] It has also been observed that the presence of these monolayers lowers the coefficient of friction in tribological contact. However these same contacts cause rapid degradation of these monolayers.[2] The loss of the monolayers contributes to an increase in the adhesive contact force and leads directly to device failure whether it be unpredictable operation of the device or complete cessation of movement. This study reports on degradation of (tridecafluoro-1,1,2,2-tetrahydrooctyl)tris(dimethylamino)-silane (FOTAS) monolayers on normal as well as sliding contacts in MEMS interfaces. The degradation of the monolayer in the normal loading case was probed by measuring the change in adhesive force of the contact over the course of 300,000 normal loading cycles. In the sliding experiment a decrease in oscillation amplitude was used to probe the status of the monolayer. The onset of monolayer degradation was observed in the normal contacting experiment after approximately 80,000 normal contacting cycles, while in the case of sliding degradation was observed almost instantaneously. Work funded by the AFOSR Extreme Friction MURI and Sandia National Labs MESA Project. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000.

[1] Srinivasan, U., Houston, M.R., Howe, R.T., Maboudian, R., "Alkyltrichlorosilane-Based Self-assembled Monolayer Films for Stiction Reduction in Silicon Micromachines", Journal of Microelectromechanical Systems 1998, 7, 252-260.

[2] DePalma, V., Tillman, N., "Friction and Wear of Self-Assembled Trichlorosilane Monolayer Films on Silicon", Langmuir 1989, 5, 868-872.

Tribology

Room: 617 - Session TR2+BI+NS+MN-ThM

Biolubrication, Sensing and Adhesion

Moderator: R.W. Carpick, University of Pennsylvania

8:00am **TR2+BI+NS+MN-ThM1 Resonant Nanomechanical Sensors for Protein Detection**, ***P.S. Waggoner***, *H.G. Craighead*, Cornell University

Micro- and nanoelectromechanical systems (MEMS and NEMS) are of interest in sensing applications due to their high sensitivity, label-free operation, and potential for mutilplexed detection on a single chip. Resonant MEMS and NEMS devices have demonstrated detection of masses on the order of femtograms or less, transducing changes in mass into changes in resonant frequency. Appropriate functionalization of the sensor surface allows specific, label free detection for analytes of choice. In this work we have detected prostate specific antigen (PSA), a biomarker used in the early detection of prostate cancer, as a model system using immunospecific functional layers present on the resonator surfaces. We have also studied the surface chemistry in order to minimize non-specific binding during sensor functionalization and use. In addition, sandwich assay techniques have been investigated for use in secondary mass tagging in order to enhance sensor response for dilute analytes while still preserving specificity.

8:20am **TR2+BI+NS+MN-ThM2 Correlation between XPS Data and Liquid Phase Self-Assembly of Alkanethiols**, ***H.M. Meyer III***, *T.G. Thundat*, *R. Desikan*, Oak Ridge National Laboratory, *R.G. White*, Thermo Fisher Scientific, UK

The relative ease in which self-assembled monolayers (SAM) can be applied have made them part of the standard tool set used for functionalizing and patterning surfaces at the nanoscale. Recently, alkanethiol-based SAMs have been used for immobilizing selective chemical receptors on the gold-coated side of a microcantilever. In this configuration, adsorption on the funtionalized side of the microcantilever generates nanomechanical motion (i.e. bending) which can be accurately sensed and used for detecting a variety of chemical and biological molecules. Achieving reliable selectivity and sensitivity depends primarily on the reproducible formation of the functional layer on one side of the microcantilever. We have recently investigated the effect of chain length on the packing density of the alkanethiols and, in turn, how this affects the sensitivity of the sensor. We present XPS characterization of microfabricated cantilevers functionalized with alkanethiol-based SAMs. The results are correlated with similar cantilevers that have been monitored during adsorption/immobilization of the same alkanethiols in the liquid phase. Previous liquid phase results indicated an unusual change in packing density of the thiol molecules as the chain length was increased and were difficult to correlate with preliminary XPS data, indicating major difference between how these films form in liquid phase vs. post-formation analysis in-vacuuo. These new results attempt to illuminate those differences. Research sponsored in part by grant NSF Award ID 0330410 in collaboration with Drs. V.P. Dravid, G. Shekhawat, and A. Majumdar and in part by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of FreedomCAR and Vehicle Technologies, as part of the High Temperature Materials Laboratory User Program, Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U.S. Department of Energy under contract number DE-AC05-00OR22725.

8:40am **TR2+BI+NS+MN-ThM3 Surface-Chemical Aspects of Implant Biotribology and Biomimetic Lubrication**, ***N.D. Spencer***, ETH Zurich, Switzerland **INVITED**

Following implantation of a hip prosthesis, the synovial membrane reforms and generates a liquid, pseudo synovial fluid (PSF), which is comparable in composition to synovial fluid itself. This complex solution of proteins, glycoproteins, polysaccharides and lipids is then responsible for the lubrication of the implanted joint. Surprisingly, the interactions of PSF components with the surfaces of joint materials, such as UHMWPE, CoCrMo, or alumina, remain remarkably unexplored. Not only is their relative propensity for adsorption unknown, but, once adsorbed, their efficacy for lubrication remains to be determined. We have investigated these issues by means of tribometry (on both macro and nano scales), combined with fluorescence microscopy, and determined, for example, that while albumin, the major component of PSF and the model protein used for implant testing, is strongly adsorbed on the surface of implants, it can be displaced during sliding by Î±-glycoprotein, a species present at much lower concentrations, but a much more effective lubricant. The fluorescence approach has also enabled us to detect transfer of polyethylene under conditions where it was not previously thought to occur. Natural lubricated surfaces tend to be soft and covered with species such as polysaccharides that have the ability to retain large amounts of water. We have attempted to imitate and understand this mechanism of lubrication by means of tethering various highly hydrated polymer chains in a brush-like structure onto both hard and soft surfaces and measuring their tribological properties. Interestingly, on soft surfaces, the effect of chain tethering seems to be to effectively eliminate boundary lubrication entirely. Fluid-film-like behavior is thought to persist to very low sliding speeds, by virtue of water retention in a thin layer between the brush-covered surfaces.

9:20am **TR2+BI+NS+MN-ThM5 In-situ Measurement of Boundary-Lubrication on Articular Cartilage Surfaces**, *J.M. Coles*, Duke University, *G.D. Jay*, Brown University, *F. Guilak*, ***S. Zauscher***, Duke University

The diarthrodial (synovial) joints of the body enable locomotion and activity while withstanding millions of cycles of loading at several times body weight. Recent macroscopic tribological experiments and biochemical analyses suggest that heavily glycosylated proteoglycans encoded by the gene proteoglycan 4 (Prg4), which are expressed by synoviocytes in synovial fluid as lubricin and by superficial zone chondrocytes of articular cartilage as surface zone protein (SZP), provide boundary lubrication in cartilage in the absence of interstitial fluid pressurization. Improved understanding of the role of Prg4 on the cartilage surface could thus provide important insight into the development of new therapies for joint diseases such as OA. The development of powerful new methods for the genetic manipulation of mice has led to the creation of modified murine strains in which specific gene inactivation (PRG4-/-) results in age-related joint degeneration that recapitulates the symptoms of OA. Here we show that atomic force microscopy with a colloidal probe is uniquely suited to study boundary lubrication of murine cartilage in-situ and in absence of other lubrication mechanisms. Here we report on friction measurements on the superficial surface layer of articular cartilage from the femoral head of Prg4 knockout and wildtype mice under boundary lubrication conditions. Furthermore, we report on the measured RMS roughness and Young’s modulus to quantify morphological and mechanical changes of the cartilage superficial zone induced by the absence of Prg4. Our measurements suggest that the absence of Prg4 leads to increased friction, as well as degradation of the mechanical and topographical properties of cartilage. We propose that, while lubricin plays a role as a boundary lubricant, its role in chondroprotection is equally, if not more, vital.

9:40am **TR2+BI+NS+MN-ThM6 Humidity Dependent Ordering of Water and its Effect on Adhesion and Friction between Silica Surfaces**, ***B.I. Kim***, *J. Bonander*, Boise State University

Adhesion and friction related to water are major problems limiting both the fabrication and long-term use of micro-machines. Adhesion and friction between two silica surfaces were measured as a function of separation distance using interfacial force microscope (IFM) for different relative humidity (RH) between 3% - 78%. The IFM provides force-distance curves without having the "snap-to-contact" problems associated with atomic force microscopy using voltage-controlled force feedback. The measured friction force-distance curves show that the friction force is oscillatory as the separation changes below thickness of water droplet. The oscillatory period is close to the mean diameter of a water molecule. The number of oscillation increased as the relative humidity increases up to RH 60% while it decreased with humidity above RH 60%. The origin of the oscillatory feature in the "interfacial" water may come from the "solid-liquid transition" between solid (ordering) and liquid (disordering). Strong correlation between the number of oscillation and the strength of the adhesion and friction indicates that the humidity dependent adhesion and friction may be attributed to the ordered structure of water molecules between two silica surfaces.

10:00am **TR2+BI+NS+MN-ThM7 Nanomechanical Properties of Arachidic Acid Langmuir Blodgett Films**, ***G. Oncins***, University of Barcelona, Spain, *J. Torrent-Burgues*, Universitat Politecnica de Catalunya, Spain, *F. Sanz*, Universitat de Barcelona and Center of Nanobioengineering of Catalonia (IBEC), Spain

Scanning Probe Microscopies development has given biophysics the possibility to deal with the interactions arisen in biological membranes from a nanomentric point of view, revealing that van der Waals, hydrogen bonding and electrostatic interactions play a crucial role in the membrane cohesion. Unfortunately, although interesting experimental conclusions have been reported in the past, these systems are complex and difficult to study.[1] In order to isolate the effect of the different cohesive interactions, Langmuir-Blodgett (LB) fatty acid monolayers provide excellent model systems because of the controlled area per molecule, linear hydrocarbon chain geometry, amphiphilic nature, high mechanical stability and the possibility to test solid and liquid phases at room temperature. The nanomechanical properties of arachidic acid LB films extracted at surface pressures of 1, 15 and 35 mN/m and deposited on mica are investigated by Atomic Force Microscopy, Force Spectroscopy and Friction Force Microscopy. It is experimentally demonstrated that the molecular ordering depends on the extraction pressure, while discrete molecular tilting angles of 50°, 34° and 22° are detected and identified as conformations that maximize van der Waals interactions between alkyl chains. The vertical force (F_v) needed to puncture the monolayer strongly depends on the molecular tilting angle, ranging from 13.07±3.24 nN at 1 mN/m to 22.94±5.49 nN at 35 mN/m. The friction force (F_f) measurements performed from low Fv until monolayer disruption reveal three friction regimes corresponding with a low F_f elastic monolayer deformation at low F_v, followed by a sharp increase in F_f due to a sudden plastic deformation of the monolayer. The last regime corresponds with the monolayer rupture and the contact between tip and substrate. Interestingly, as the extraction pressure increases, the friction coefficient of the monolayer reduces while the F_v needed to trigger the monolayer plastic deformation increases, facts that are discussed in terms of sample compactness and monolayer rupture mechanism.[2]

[1] Garcia-Manyes, S.; Oncins, G.; Sanz, F. Biophys. J. 2005, 89, 1812.

[2] Oncins, G.; Garcia-Manyes, S.; Sanz, F. Langmuir 2005, 21, 7373.

10:20am **TR2+BI+NS+MN-ThM8 Optimal Roughness for Minimal Adhesion**, *D.L. Liu,* Worcester Polytechnic Institute*, J. Martin,* Analog Devices Inc.*, **N.A. Burnham***, Worcester Polytechnic Institute

Differing views on the effect of surface roughness on adhesion have appeared in the literature recently. Molecular dynamics has been used to simulate the contact of two surfaces and found that atomic-scale roughness can have a large influence on adhesion, causing the breakdown of continuum mechanics models.[1] An experimental study showed that roughness can determine the adhesion in nanometer contacts and indicated that continuum mechanics still works down to nanometer length scales.[2] In this work, we use a single-asperity model to describe a smooth tip in contact with a rough surface and predict that there is an optimal size of asperity that will yield a minimum of adhesion. Experimentally, adhesive forces on silicon wafers with varying roughness from 0.2 nm to 39 nm were measured using AFM (atomic force microscope) cantilevers with varying tip radii ranging from 75 nm to 9.08 um. It is found that for all tip radii, the adhesion falls significantly for roughness greater than 1-2 nm and drops at higher roughness for larger tips. Minimum adhesion was observed as predicted in the 1-10 nm range and the optimal roughness for minimal adhesion increases as the tip radius increases, which is also consistent with our predictions. The work presented here should help minimize adhesion in future MEMS devices and progress the understanding of adhesion between the atomic- and macro-scale.

[1] B. Luan and M.O. Robbins, Nature 435, 929-932 (2005).

[2] E.J.Thoreson, J. Martin, N.A. Burnham, J. Colloid Interface Sci. 298, 94-101 (2006).

10:40am **TR2+BI+NS+MN-ThM9 A Tribological Study of Bound plus Mobile Lubricants for MEMS Application from the Nano- to the Macro-scale Regime**, ***B.P. Miller****, M. Brukman,* North Carolina State University*, C.C. Baker,* Naval Research Laboratory*, R.J. Nemanich,* North Carolina State University*, K.J. Wahl,* Naval Research Laboratory*, J. Krim*, North Carolina State University

One possible solution to the in-use stiction problem in Micro-Electro-Mechanical systems (MEMS) is the introduction of a bound plus mobile lubricant combination.[1] For this system, one monolayer of the bound lubricant (perfluorodecyltrichlorosilane, PFTS) bonds to the surface of the device. The mobile lubricant (tricresyl phosphate, TCP) can replenish the layer after rubbing contacts wear it away, thus keeping the device free of contamination. Friction behavior of this lubricant combination was examined over three different regimes using a macroscopic tribometer, an AFM, and a quartz crystal microbalance (QCM). A comparative study of bound only versus bound plus mobile lubricants showed a decrease of the coefficient of friction with the addition of the mobile lubricant to the bound layer. Dynamic properties of the mobile film were characterized with the QCM. This work is funded by AFOSR Extreme Friction MURI Grant #FA9550-04-1-0381.

[1] W. Neeyakorn, M. Varma, C. Jaye, J. E. Burnette, S.M. Lee, R. J. Nemanich, C. Grant, J. Krim, Dynamics of Vapor-Phase Organophosphates on Silicon and OTS, Tribology Letters, in press.

Tribology

Room: 617 - Session TR3+NS-ThA

Nanotribology and Nanomechanics

Moderator: P.R. Norton, University of Western Ontario, Canada

2:00pm **TR3+NS-ThA1 Quantitative Direct-Observation Nanomechanical Testing in the Transmission Electron Microscope**, ***O.L. Warren***, *Z. Shan, S.A.S. Asif,* Hysitron, Inc., *E.A. Stach,* Purdue University, *A.M. Minor*, Lawrence Berkeley National Laboratory **INVITED**

The increasingly strong interest in measuring and understanding the sometimes extraordinary mechanical properties of nanomaterials and individual nanostructures has encouraged us to develop the first depth-sensing indenter compatible with quantitative nanomechanical testing in the transmission electron microscope (TEM). This ambitious undertaking has encountered a number of significant technological hurdles to overcome; nevertheless, we have achieved a versatile in-situ TEM instrument that compares favorably to leading conventional nanoindenters in terms of control modes and performance specifications. Scientifically, we have exploited the unique capabilities of this novel instrument to perform direct-observation nanoindentation into thin films and monolithic materials using sharp indenters, direct-observation nanocompression onto hollow and solid nanospheres as well as onto crystalline and amorphous nanopillars using miniature flat punches fashioned with a focused ion beam (FIB), and direct-observation bending of nanowires using the aforementioned flat punches. This presentation will share the powerful nature of time correlating the often discrete features of force-displacement curves to the accompanying morphological and microstructural changes that are directly observed in the corresponding TEM movies. Our research results range from some validating current mechanistic thinking to others that are counterintuitive and therefore a challenge to conventional wisdom.

2:40pm **TR3+NS-ThA3 Tribology in Full View**, ***L.D. Marks***, *A. Merkle*, Northwestern University **INVITED**

Experiments in tribology have long suffered from the inability to directly observe what takes place at a sliding contact - the classic buried interface problem. As a consequence, although many friction phenomena at the nanoscale have identified, there can be interpretation issues resulting from indirect or ex-situ characterization of the contact surfaces or because the experimental measurements are volume averaged, rather than giving direct insight into what is taking place at a single asperity-asperity contact. We have been recently exploiting a unique instrument that allows us to simultaneously slide a tip across a surface and look at the sample using transmission electron microscopy. Using this technique, we can directly image the nanoscale processes taking place at scales from 0.2 nm to microns, as well as obtain local chemical information from techniques such as electron energy loss spectroscopy. Using this instrument we have recently observed "liquid-like" deformation where the material is solid, but behaves as if it was a liquid due to very rapid surface diffusion, similar to the classic case of liquid-like growth of gold and silver particles; the formation of a graphitic transfer layer during sliding of tungsten on graphite as well as in-situ observation of graphitization of diamond-like carbon during sliding observed by electron energy loss spectroscopy. Further results include observation of wear debris during sliding of tungsten on graphite whose size is consistent with a dislocation standoff model and a recently published dislocation model for friction at the nanoscale. These and additional results will be described.

3:40pm **TR3+NS-ThA6 Atomic-scale Friction on Ultra Thin Films**, ***T. Filleter***, *W. Paul, R. Bennewitz*, McGill University, Canada

Friction force microscopy (FFM) provides a powerful method to study the microscopic origins of friction. FFM has previously demonstrated that a single sharp asperity scanned over an atomically flat crystalline surface can exhibit a periodic stick-slip movement following the periodicity of the underlying lattice.[1] This has been observed for a range of different crystalline surfaces, including alkali halides and metal single crystals.[2,3] In this work we have extended the FFM technique to study atomic-scale friction on a model solid lubricant system. The system was chosen to satisfy two criteria; be composed of materials with well known bulk atomic frictional properties, and to be topographically well defined with atomic resolution. The model system, which satisfies both criteria, are ultra thin films of KBr grown on a single crystal Cu(100) substrate. Ultra thin films have been grown under ultra high vacuum conditions with a thickness of up to five monolayers of KBr on an atomically flat Cu(100) substrate. The films have first been characterized using high resolution noncontact atomic force microscopy (NC-AFM). The first and second monolayers are found to grow in a carpet-like mode overtop of the existing Cu monatomic steps. Subsequent layers grow as rectangular islands with a minimum of corner and kink sites. Atomically resolved NC-AFM topography images of the films reveal a regular superstructure in the growth which is consistent with the KBr/Cu lattice mismatch. FFM measurements show that, as expected, the KBr films do act as a solid lubricant exhibiting lower friction than the bare Cu(100) surface. It is also observed that layers with a thickness of two and greater monolayers supports stable atomic stick-slip friction. The atomic frictional properties on films as thin as two monolayers (0.66 nm) are found to be consistent with that of bulk KBr. Lateral force maps of films exhibiting a topographic superstructure do not reveal a superstructure in the lateral force. The bare Cu(100) substrate has also been found to support stable stick-slip friction which has previously not been achieved.

[1] Bennewitz, R., Materials Today, May 2005, p.42

[2] Socoliuc, A., et. al, Phys. Rev. Lett. 92, 13 (2004) 134301/1-4

[3] Bennewitz, R., et. al, Phys. Rev. B 60, 16 (1999) R11301-4.

4:00pm **TR3+NS-ThA7 A Scanning Tunneling Microscope and Quartz Crystal Microbalance Study of Heating and Wear at a Sliding Interface**, ***B.D. Dawson***, *S.M. Lee, J. Krim*, North Carolina State University

In order to probe the rise in temperature of a sliding interface, a Scanning Tunneling Microscope and Quartz Crystal Microbalance has been combined to produce a rubbing action of a tungsten tip on a copper and indium electrode, respectively. The amplitude of oscillation[1] and wear of the electrodes is observed directly with the STM. Negative frequency shifts, which are indicative of a liquid-solid interface,[2] were observed for tungsten on indium rubbing. The chamber was heated and negative frequencies were observed at reduced sliding speeds, implying surface melting at the indium interface. This work was funded by The National Science Foundation and the AFOSR Extreme Friction MURI.

[1] B. Borovsky, B. L. Mason, and J. Krim, J. Appl. Phys. 88, 4017 (2000).

[2] C. M. Flanigan, M Desai, and K. R. Shull, Langmuir. 16, 9825 (2000).

4:20pm **TR3+NS-ThA8 Radial Breathing Mode Frequencies of Single-Walled Carbon Nanotubes Determined by Nanoindentation with an AFM**, ***J. Fraxedas***, ICMAB-CIN2-CSIC, Spain, *G. Rius, F. Pérez-Murano,* IMB-CNM-CSIC, Spain, *A. Verdaguer*, ICN-CIN2, Spain

We have experimentally determined the radial breathing mode frequency of individual single-walled carbon nanotubes with a diameter of 1.3 nm by nanoindentation measurements using an Atomic Force Microscope with commercial microfabricated silicon cantilevers with ultrasharp tips, evidencing the sensitivity of such instruments to frequencies in the THz range, well above the resonance frequencies of the cantilevers (ca. 130 kHz).[1]

[1] Europhys. Lett. 78 (2007) 16001.

4:40pm **TR3+NS-ThA9 The Importance of Nanoscale Meniscus Formation During High-Speed Sliding Contacts**, ***C.M. Mate***, *R.N. Payne, Q. Dai,* Hitachi San Jose Research Center, *K. Ono*, Hitachi Central Research Laboratory, Japan

To help determine the nanoscale origins of friction at high-speed sliding contacts, we have developed a High Shear Rate Apparatus using technology from the disk drive industry. This technique enables us to study friction, adhesion, and wear at ultra-high sliding speeds (1 to 100 m/s) for a small pad contacting a rotating disk with an atomically smooth surface and covered with a nanometer thick lubricant film.[1] We find that the sliding characteristics are dominated by the non-equilibrium meniscus of lubricant that forms between the pad and disk surfaces and by the vibrational dynamics of the sliding interfaces. In particular, the high sliding speed results in the friction, adhesion, and bounce dynamics being asymmetric with respect to sliding direction for a pad tilted at a slight angle with respect to the rotating disk surface. These differences are attributed to the mechanical action of the lubricant layer against the converging and diverging wedges of the pad, leading to an asymmetric meniscus to form around the contact pad at high speeds. Under suitable conditions, we also find a self-excited vibration of the slider pad, a few nanometers in amplitude, which is induced by friction hysteresis coupled with adhesion hysteresis.

[1] C. M. Mate, R.N. Payne, Q. Dai, and K. Ono, "Nanoscale Origins of Dynamic Friction in an Asymmetric Contact Geometry", Phys. Rev. Lett. 97 (2006) 216104.

5:00pm **TR3+NS-ThA10 Effects of Interfacial Structure on Atomic-Scale Friction Examined using MD**, ***J.A. Harrison***, *M.T. Knippenberg, J.D. Schall, G. Gao, P.T. Mikulski*, United States Naval Academy

The development of micron-sized devices, such as microelectromechanical devices, for terrestrial and space applications has prompted the need for protection of the surfaces of these devices. Self-assembled monolayers (SAMs), both alkanethiols and alkylsilanes, are possible candidate for the passivation and lubrication of these devices. The fundamental problem associated with controlling friction is a lack of understanding of the underlying atomic-scale processes that govern both friction and wear. We have conducted extensive molecular dynamics (MD) simulations using our AIREBO potential aimed at understanding the atomic-scale mechanisms of friction in SAMs. We have examined the way in which the contact forces present at the interface influence friction and made direction connections between interfacial structure and friction. We have examined the effects of changing the interface structure in several ways. Some of these include changing the structure of the SAM (e.g., end-group, chemical identity, hybridization, connectivity of chains) and altering the roughness of the interface. In this talk, we will discuss our most recent findings that have examined the way in which the structure of both the SAM and the tip influence friction. ** Work supported by The Office of Naval Research and The Air Force Office of Scientific Research as part of the Extreme Friction MURI.

Tribology

Room: 617 - Session TR4+SE-FrM

Friction and Wear of Engineered Surfaces Macro- to Nanoscale Approaches

Moderator: N.D. Theodore, Naval Research Laboratory, North Carolina State University

8:00am **TR4+SE-FrM1 Mechanical, Chemical, and Tribochemical Etching of Silicon Studied by Atomic Force Microscopy[1]**, ***F. Stevens***, *S.C. Langford, J.T. Dickinson*, Washington State University

Commercial silicon nitride tips for atomic force microscopy (AFM) were used as model asperities to study the mechanical and tribochemical wear of a Si(110) surface. Aqueous sodium hydroxide and tetraethyl ammonium solutions were employed as chemical etchants. Under these conditions, tip wear is a significant issue; a new tip was employed for each wear measurement. Changes in tip contact stress were estimated by characterizing tip shapes before and after wear. In basic solution, the native oxide can be patterned by the AFM tip to expose the more vulnerable underlying Si to the chemical etchant.[2] Features 20 nm deep, with lateral dimensions less than 100 nm, are readily produced. The rate of oxide wear is a strong function of force applied to the AFM tip; even at low contact forces, scanning significantly accelerates oxide wear. Initial penetration of the native oxide is not uniform and produces deep pits—presumably at pinholes or similar defects in the oxide. Once the oxide is fully penetrated in the scanned region, subsequent tribochemical etching produces depressions with flat, smooth bottoms. For a given contact force and solution, the final wear depth relative to the surrounding, chemically etched material depends only on the number of times the AFM tip has passed over the surface; changing the tip velocity has no significant effect. Thus the tribochemical component of wear is not limited by chemical reaction rates under the conditions of this work. To characterize mechanical wear apart from chemical effects, hydrogen-terminated Si surfaces were scanned in inert solutions and atmospheres; images after wear in argon show wear debris, consistent with abrasive wear. The observed abrasive wear is sufficient to account for 5-10% of the Si wear observed in the presence of basic solution. Tribochemical effects during Si wear at a contact force of 300 nN in 0.1 M NaOH can easily enhance the total etch rate by a factor of two over the sum of the chemical and mechanical wear rates.

[1] This work was supported by the US National Science Foundation under Grant CMS-0409861.

[2] S. Miyake and J. Kim, Nanotechnology 16, 149 (2005).

8:20am **TR4+SE-FrM2 New Techniques for the Quantitative Determination of nm/hr Wear Rates of Materials**, *P.R. Norton, G. Pereira,* ***Y.-R. Li,*** University of Western Ontario, Canada, *A. Lachenwitzer,* Cameco Corporation, *A. Alpas,* University of Windsor, Canada, *W. Capehart*, General Motors

Much effort has been spent on the chemical and mechanical characterization of antiwear films formed from ZDDP additives in automobile engines and on the mechanisms of their formation. By contrast, much less effort has been devoted to evaluating the wear itself. This is largely because the wear rates required in the engine are of order nm/hr, and accelerated testing under high loads is unacceptable because of the ubiquity of wear-rate transitions which make extrapolation to low loads difficult or impossible. The absence of relevant low-load (ultra-mild) wear data means that it is currently not generally possible to correlate the film characterization and wear rate studies, creating a huge gap in our understanding of wear. We are addressing this unsatisfactory situation by developing new techniques for directly measuring wear rates down to nm/hr in tests lasting a few hours. These techniques must be capable of measuring both the initial and long-term wear rates, be valid in the presence of surface films and take account of retention of material during wear. The strategy involves the implantation of Au atoms into the near-surface 100 nm region of a material (currently 52100 steel or an Al-Si alloy), and the determination of the loss of gold from the samples by means of Rutherford Backscattering (RBS) and Heavy Ion Backscattering (HIBS), and the accumulation of gold in the lubricant by Neutron Activation Analysis (NAA). The initial profiles can be either uni-modal or multi-modal with depth, to provide sensitivity to short and long-term behaviour. The analysis of both sample and lubricant/debris quantitatively accounts for all implanted gold, and the depth resolution of HIBS permits determination of the location of the residual gold in the samples.

8:40am **TR4+SE-FrM3 Nano-scale Friction and Wear of Carbon-Based Materials**, ***R.W. Carpick***, University of Pennsylvania, *D.S. Grierson, A.R. Konicek, P.U.P.A. Gilbert,* University of Wisconsin-Madison, *A.V. Sumant, O. Auciello,* Argonne National Laboratory, *R.J. Cannara,* IBM Zürich, Switzerland, *T.A. Friedmann,* Sandia National Laboratories, *W.G. Sawyer,* Univeristy of Florida, *J.A. Carlisle*, Advanced Diamond Technologies **INVITED**

Nanostructured carbon-based materials, such as nanocrystalline diamond and atomically smooth, nanometer-thick diamondlike carbon films, have outstanding and in many cases unrivalled tribo-mechanical properties. The atomic structure of the surfaces, verified by detailed surface spectroscopy, critically affects nano-scale friction and adhesion. We will specifically discuss how hydrogen termination, sp2-content, and crystal orientation affect adhesion and friction at the nanoscale. Next, we discuss how surface spectroscopy and imaging can be simultaneously applied to study wear of carbon films using photoelectron emission microscopy (PEEM)/X-ray absorption near edge structure (XANES). From these studies we test the hypotheses of ultralow friction in these materials, specifically, the extent to which chemical passivation of dangling bonds and convertion to graphitically bonded carbon occur. Finally, we will discuss taking advantage of this knowledge for nanoelectromechanical systems and advanced nanoprobe applications.

9:20am **TR4+SE-FrM5 Wear in MEMS-Based Microball Bearings**, ***B. Hanrahan***, *M. McCarthy,* University of Maryland, *C. Zorman,* Case Western Reserve University, *A.V. Sumant,* Argonne National Laboratory, *R. Ghodssi*, University of Maryland

PowerMEMS devices supported on microball bearings have been successfully demonstrated at low operating speeds. Continued research on the tribological properties of these support structures is necessary for the realization of robust high-speed devices. Critical dimensions need to be maintained within tight tolerances when operating high speed micromachines. The wear between stationary and moving elements must, therefore, be minimized to reduce the change in critical dimensions over the lifetime of the device. Accordingly, the mechanism of wear between silicon and hardened steel microballs is the focus of this work. Silicon test structures, 23 mm in length, were fabricated with 300 µm wide deep-etched rectangular trenches acting as housings for the microballs. The 285 µm steel balls were sandwiched between two test structures under an applied normal loading. Oscillatory motion is generated between the two structures using an externally controlled stepper motor at 400 rpm and a traveling distance of 4mm. At periodic time intervals, the test device is disassembled and inspected using an optical profilometer to determine changes in the surface topography. To the best of our knowledge, this is the first investigation of wear in MEMS-fabricated ball bearings. Initial results show both deposition and removal of material within the microfabricated trenches. At 50,000 cycles, equivalent to 200 meters of travel, an increase in average surface roughness from 7.5 nm to 30.2 nm is observed. These results suggest the adhesion and subsequent shearing of contacting materials, increasing the overall roughness. The properties of the mating materials play a critical role in determining the wear mechanism. To expand the scope of the study, solid thin film lubrication has been explored. Silicon carbide and ultra-nanocrystalline diamond are ideal candidates for wear resistant films because of their high hardness, low interfacial energy, and compatibility with MEMS fabrication processes. In our analysis we will present a detailed investigation of the wear mechanisms of steel balls on silicon with and without solid lubrication.

9:40am **TR4+SE-FrM6 Microstructure and Tribological Behavior of W-DLC Coated Rubbers**, ***Y.T. Pei,*** *X.L. Bui,* University of Groningen, the Netherlands, *X.B. Zhou,* SKF Research and Development B.V., the Netherlands, *J.T.M. De Hosson*, University of Groningen, the Netherlands

W-DLC coatings have been deposited on FKM, ACM and HNBR rubbers via unbalanced magnetron reactive sputtering from a W target in C_2H_2/Ar plasma. The surface morphology and fracture cross sections of uncoated and coated rubbers are characterized with high resolution SEM. The tribological behaviors of uncoated and coated rubbers have been investigated with ball-on-disc tribotest under dry sliding against 100Cr6 ball. The coefficients of friction (CoF) of uncoated rubbers are very high ($\mu > 1$). Relatively high CoF of W-DLC coated FKM (about 0.6) is observed due to the gradual fracture and delamination of the coatings. In contrary, W DLC coated HNBR rubbers exhibit superior tribological performance with a very low CoF of 0.2-0.25 (comparable to that of Me-DLC coatings deposited on steel substrates). After 10000 sliding laps, almost no damage of the coatings is observed on the wear tracks. The micro-crack networks as deposited facilitate the flexibility of the coatings. The different surface roughness and mechanical properties of the rubber substrates explain the differences in the tribological performances of the coated rubbers. For soft and flexible substrates such as rubbers, metallic interlayer does not enhance the interfacial adhesion but negative effects are observed.

10:00am **TR4+SE-FrM7 Adaptive Tribological Nanocomposite Coatings**, ***C. Muratore***, *J.J. Hu, A.A. Voevodin*, Air Force Research Laboratory **INVITED**

Plasma processing allows precise control of the composition, microstructure and architecture of nanocomposite coating materials, enabling the design of materials that automatically adapt to variable aerospace environments, including humid and dry ambient air, space, and high temperature oxidizing conditions. Self-adaptive materials are of particular interest in tribological applications because most solid lubricants are effective in only a narrow range of ambient conditions. Thoughtful selection of multiple solid lubricant phases and the development of novel lubricant delivery mechanisms such as controlled diffusion, catalysis and chemical reactions with the surrounding atmosphere enhanced by contact between moving surfaces have recently been realized to achieve adaptation in diverse environments. For example, nanocomposite yttria-stabilized zirconia (YSZ) coatings containing Ag, Mo and other nanosized inclusions depend on temperature-activated adaptations to yield low friction (<0.2) from 25-700 °C in air. For YSZ-Ag-Mo nanocomposites, lubrication below 500 °C results from diffusion and coalescence of silver at the surface. Above 500 °C, the silver is pushed out of the wear contact, exposing a limited quantity of molybdenum in the coating to air, and initiating the controlled formation of MoO_3 and other compounds exhibiting low shear strength and thus easy sliding at high temperatures. While these adaptations at the surface reduce friction, irreversible compositional and structural changes resulting from the migration of film components can compromise the mechanical properties of the coating, thus reducing its utility over long periods at high temperature or through multiple thermal cycles. Moreover, some lubrication mechanisms occur over the entire coating surface in addition to the area experiencing wear, thus wasting the limited quantity of lubricious material stored in the coating. Coating architectures that control adaptation rates or selectively inhibit adaptation on coating surfaces unaffected by wear have been developed to increase the lifetime of adaptive tribological materials. Additionally, smart coatings with wear sensing capability have been developed to facilitate coating development and to improve reliability in critical applications.

10:40am **TR4+SE-FrM9 Hard Nanostructured Sulfur-Doped CHx-TiB2 Coatings for Improved Friction and Mechanical Performance**, ***B. Zhao***, *Y.W. Chung*, Northwestern University

Hydrogenated amorphous carbon films are known to attain ultra-low friction performance only in dry environments. Our work demonstrated that sulfur doping of hydrogenated carbon films results in ultra-low friction performance in both dry and humid environments. However, these films have a hardness of 7 - 10 GPa and an elastic modulus around 80 GPa, which are too low for some high stress applications. Formation of nanolayer or nanocomposite coatings is known to improve hardness. With the aim to produce hard, low-friction coatings, we synthesized nanostructured films of sulfur-doped hydrogenated carbon and titanium diboride using dual-target magnetron sputtering. This paper will discuss the film structure and how such structure correlates with its tribological and mechanical properties.

11:00am **TR4+SE-FrM10 The Relation of Hydrogen to Superlubricity of DLC Films**, ***O.L. Eryilmaz***, *A. Erdemir*, Argonne National Laboratory

In this study, we investigated the critical role of hydrogen in friction and wear mechanisms of hydrogen-free and -poor films in dry nitrogen and high-vacuum environments. Using TOF-SIMS and XPS, we found a very important relationship between friction coefficient and the degree of hydrogenation in these films. Specifically, friction and wear test results showed that the films grown in hydrogen-free or -poor plasmas, the friction coefficients were very high (more than 0.5)and un-steady; and these films wore of very quickly during the sliding tests. However, when these films were subjected to very short-duration (a few minutes) post-hydrogen plasma treatment, their friction coefficients became very low (i.e., less than 0.1) and they were able to last very long during sliding tests. Surface analytical characterizations of the films and sliding contact surfaces were done using XPS and TOF-SIMS as well as Raman Spectroscopy and the chemical and structural findings were correlated with the tribological performance of the films. In particular, TOF-SIMS results revealed very close relationship between surface chemistry and tribological performance of DLC films.

11:20am **TR4+SE-FrM11 Friction and Wear Properties of Nanocrystalline Diamond Coatings**, ***C.C. Baker***, *N.D. Theodore*, Naval Research Laboratory, *T. Feygelson*, GeoCenters Incorporated, *J.E. Butler, K.J. Wahl*, Naval Research Laboratory

The tribological behavior of nanocrystalline diamond (NCD) coatings was studied under both unidirectional and reciprocating sliding conditions. Coatings were deposited by microwave plasma chemical vapor deposition onto Si substrates under varying growth conditions to thicknesses between 1-2 microns. Friction behavior was investigated using pin-on-flat geometry with sapphire counterfaces at average contact pressures of 0.43-0.74 GPa. Wear volumes of the ball counterface and coating wear tracks were determined with optical interferometry. Coating microstructure, chemistry, and surface morphology were examined using X-ray diffraction (XRD), micro-Raman spectroscopy, and atomic force microscopy (AFM). We have found that friction coefficients for the sapphire-NCD sliding interface are low, ranging from 0.03 to 0.1. However, there were large differences in friction run-in, with run-in from high to low friction taking between 50 to as many as 10000 cycles over a wide range of NCD deposition conditions. The role of coating microstructure, bonding chemistry, wear, and roughness of worn and unworn surfaces on run-in friction behavior of NCD will be discussed.

11:40am **TR4+SE-FrM12 Effects of Annealing on Anti-Wear and Anti-Bacteria Behaviors of TaN-Cu Thin Films**, ***J.H. Hsieh***, *M.K. Cheng, Y.K. Chang*, Mingchi University of Technology, Taiwan, *S.H. Chen*, National Chiayi University, Taiwan, *P.C. Liu*, Mingchi University of Technology, Taiwan

TaN–Cu nanocomposite films were deposited by reactive co-sputtering on Si and tool steel substrates. The films were then annealed using RTA (Rapid Thermal Annealing) at 400 ?C for 2, 4, 8 minutes respectively to induce the nucleation and growth of Cu particles in TaN matrix and on film surface. C-AFM (Conductive Atomic Force Microscopy) and FESEM (Field Emission Scanning Electron Microscopy) were used to confirm the emergence of Cu nano-particles on the surface of TaN-Cu thin films. The effects of annealing on anti-wear and anti-bacteria properties of these films were studied. The results reveal that annealing by RTA can cause Cu nano-particles with various dimensions to emerge on the TaN surface. Accordingly, hardness and friction coefficients will change, as well as the anti-bacterial behavior.

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