Tuesday Afternoon, November 10, 2009

Tribology Focus Topic
Room: B2 - Session TR+SS-TuA

Surface Science for Tribology
Moderator: I. Szlufarska, University of Wisconsin, Madison

2:00pm **TR+SS-TuA1 Effect of the Surrounding Gas Pressure on Charge Separation Caused by Friction between Insulators**, ***T. Miura***, *E. Hosobuchi, S. Ueno, I. Arakawa*, Gakushuin University, Japan

Friction between insulators induces charge separation at the interface. The surface electrification after sliding contact yields electric field in the gap near the contact and results in gas discharge if the friction is carried out in a gas ambience. This gas discharge reduces the charge that was once induced at the frictional interface. It has been believed that the initial charge separation was not affected by a surrounding gas and was determined solely by the frictional materials. We have investigated the charge separation rate before the gas discharge under various gas conditions and found that it linearly decreased with the logarithm of the pressure from 10 Pa to atmospheric pressure for Ne, Ar, and Kr.

The friction experiment was performed by means of pin-on-disk equipment. The pin was made of natural diamond and was gold coated. The disk was quartz or sapphire. The charge accumulated on the gold-coated pin was measured by an electrometer. The diameter of a contact area between the bare diamond tip and the disk was about 10 μm and the sliding velocity was 11 μm/s. The charge on the pin increased at a constant rate during sliding and fell to zero when the gas discharge occurred. The charge accumulation and the gas discharge were repeated during sliding friction in a gas ambience. The initial charge density at the interface of the sliding contact was calculated from the accumulation rate, the track width and the sliding velocity.

The charge density was typically the order of 1 mC/m^2 for sliding friction in a vacuum (10 Pa). It was found that the initial charge separation under the atmospheric gas pressure is one order of magnitude smaller than that at 10 Pa. This reduction of the charge separation rate was observed for Ne, Ar, and Kr gas at almost the same efficiency. It is likely that the gas molecules penetrate into the frictional interface and interrupt or relax the charge separation. It should be necessary to investigate the surrounding gas effect on the initial charge separation in detail in order to reveal the origin of triboelectricity.

2:20pm **TR+SS-TuA2 *In situ* Tribology of Metal-Doped MoS_2: Interfacial Film Mechanics and Friction Behavior**, ***K.J. Wahl***, Naval Research Laboratory, *S.D. Dvorak*, University of Maine, *G.Y. Lee, I.L. Singer*, Naval Research Laboratory

Tribological processes that influence friction and wear involve a complex combination of materials science, physics, chemistry, and rheology. Our understanding of these sliding contact phenomena is limited by the fact that all the action takes place in a buried interface. Most often the only evaluation of these interfaces is accomplished through *ex situ* means after separating the contacts. *In situ* approaches to studying friction and wear processes are challenging because most engineerin g surfaces are metals or ceramics that have no optical transparency at visible wavelengths. For this reason, most of what is known about interfacial processes occurring during sliding has been learned through optical probes of sliding interfaces.

We have used an *in situ* tribometer to perform reciprocating sliding tests of Pb-Mo-S and Ti-Mo-S solid lubricant coatings. Experiments were performed in dry and ambient air. The interfacial films formed during sliding were monitored with *in situ* Raman spectroscopy and optical microscopy through transparent counterfaces. The dominant velocity accommodation mode in both dry and humid conditions was interfacial sliding between the surface of the wear track and the outer surface of the transfer film on the counterbody. Humid air sliding resulted in a second velocity accommodation mode involving shear and/or extrusion of the transfer film. We will demonstrate and discuss how the interface properties – shear strength and transfer film mechanical properties – affect friction behavior of these solid lubricant coatings.

2:40pm **TR+SS-TuA3 Nanosecond X-Ray Pulses From Peeling Tape in Vacuum**, ***S. Putterman***, *J.V. Escobar, C.B. Camara, J. Hird*, University of California, Los Angeles **INVITED**

That the surface between two interacting bodies can be a source of visible light –triboluminescence- has been known for centuries. Observation of the emission of nanosecond long 100.mW pulses of X-Ray photons from peeling tape indicates that tribological processes reach energy densities which are much greater than the few eV per molecule needed to generate visible photons. Analysis of the x-ray pulses indicates that they originate from micron scale regions near the vertex of peeling tape. Based upon this insight we are building a mechanically operated sub-millimeter x-ray source that can be used for medical imaging. The organized processes which transduce diffuse mechanical energy into x-ray pulses are not understood.

4:00pm **TR+SS-TuA7 Nanotribology at Cryogenic Temperatures**, ***S.S. Perry***, *X. Zhao, S.R. Phillpot, G. Sawyer, S.B. Sinnott*, University of Florida

The temperature dependence of the kinetic friction between a silicon nitride probe tip and a number of crystalline surfaces has been evaluated through atomic force microscopy measurements performed under an ultrahigh vacuum environment over the temperature range 140-750 K. Surfaces interrogated include highly oriented pyrolytic graphite, molybdenum disulfide, and lead sulfide. A relatively weak dependence on temperature is observed in the friction measured between 300 K and 750 K. As temperature decreases below ambient temperatures, a sharp increase in friction is observed for all surfaces, however with variations in the temperature threshold. Collectively, these results obtained from fundamental interfaces are consistent with an activated mechanism of energy dissipation during sliding. An Arhennius analysis of the temperature dependent friction over this range yields different effective activation energies, ranging from 0.1-0.4 eV for the thermally activated stick-slip motion of the probe tip on this surface. As temperature is reduced further, a distinct transition to a largely athermal behavior is detected and is shown to result from the onset of interfacial wear, entailing an alternative energy dissipation pathway.

4:20pm **TR+SS-TuA8 Molecular Dynamics Simulations of Nanoindentation of Si/SiO_2 Systems using the Charge Optimized Many-Body (COMB) Potential**, ***T.R. Shan***, *B. Devine, S.R. Phillpot, S.B. Sinnott*, University of Florida

Oxides and carbides, such as SiO_2, Al_2O_3, HfO_2 and SiC, are widely used together with Si in many high-performance electronic devices, including metal-oxide-semiconductor (MOS) devices/junctions and gate stacks. The lack of precise control over mechanical properties can lead to the degradation of these materials. It is therefore critical to understand the nanometer-scale mechanical properties of materials or complex systems being considered for use in electronic devices. Since nanoindentation has been established as a primary tool for investigating the mechanical behavior of small volumes of materials, classical molecular dynamics simulation is used to examine the nanoindentation of Si/SiO_2 interfacial systems. Because these systems consist of heterogeneous interface with significant changes in bonding as one crosses from one side of the interface to the other, the empirical charge optimized many-body (COMB) potential is used to model the structural evolution, mechanical response and charge transfer of Si/SiO_2 interfacial systems under the influence of a nanometer-scale indenter. The COMB potential allows for dynamic charge transfer between atoms and across interfaces, and does a good job in describing covalent and ionic bonding in these materials. Aspects of the Si/SiO_2 interface during nanoindentation, including dislocation formation and the mechanisms by which fracture occurs, will also be addressed. We gratefully acknowledge the support of the National Science Foundation through grant DMR-0426870.

4:40pm **TR+SS-TuA9 Influence of Molecular Structure and Alignment on Nanometer-Scale Tribology**, *P. Barry, P. Chiu, S.R. Phillpot,* ***S.B. Sinnott***, University of Florida

We report on the effect of small, fluorocarbon molecules on self-mated, aligned polytetrafluoroethylene (PTFE)-PTFE tribology using atomistic molecular dynamics simulations. Three fluorocarbon molecular classes were considered: C_2F_6, C_4F_{10} and C_8F_{18} with the amount of lubricant between the classes kept constant. Further, the effects of a relatively thin lubricating layer and a relatively thick lubricating layer were compared. The simulations predicted that the systems with thicker lubricating layers exhibited a friction coefficient that was significantly lower than those a thinner lubricating layer. Correspondingly, substantially more molecular wear of the PTFE surfaces were predicted for the latter systems. Interestingly, unlubricated PTFE-PTFE self-mated systems demonstrated low friction coefficients and molecular wear when the chains were slid in a direction parallel to the chain alignment, and unlubricated, aligned polyethylene (PE)-PE systems exhibited comparable or lower friction coefficients. The simulations further predicted that unlubricated, aligned PE-PTFE systems had friction coefficient values in between those of the PE-PE systems and PTFE-PTFE systems in which the chains slid in directions that were perpendicular to the alignment of the chains.

Surprisingly, the highest friction coefficients in the PE-PTFE system occurred when the chains were slid in a direction parallel to the direction in which the chains were aligned. This result was attributed to the incommensurate nature of the sliding interface between the two different polymers. This work was carried out under the support of an AFOSR MURI.

5:00pm **TR+SS-TuA10 On the Mechanical Properties of Tungsten Disulfide Nanotubes**, ***I. Kaplan-Ashiri***, *S.R. Cohen, K. Gartsman,* Weizmann Institute of Science, Israel, *G. Seifert,* Technische Universität, Germany, *H.D. Wagner, R. Tenne*, Weizmann Institute of Science, Israel

WS_2 forms multiwalled nanotubes which seem to be almost defect free and their structure can be precisely defined. Hence they can serve as good candidates for the study of nanomechanics.

Various mechanical tests were applied on individual WS_2 nanotubes to reveal their mechanical properties and behavior. First, nanotubes were axially compressed in atomic force microscope, and their Young's modulus was observed according to Euler's buckling point. An average value of 170GPa was obtained. A similar test which was conducted in the scanning electron microscope resulted in large elastic deformation of the nanotube. Here the Young's modulus was obtained from the post buckling equations, and found to be 150GPa. In a third experiment, the nanotubes were axially strained until fracture occurred. The Young's modulus was then observed according to Hooke's law and found to be 152GPa. These moduli values are in good agreement between themselves and also with density functional tight-binding (DFTB) calculations and the bulk material (150GPa).

Tensile strengths and strain values as high as 16GPa and 14% were observed as well. These values reveal that WS_2 nanotubes reached their theoretical strength, hence they are suspected to be defect free. The high strain value is unique to the tubular nanophase of WS_2 and is also in good agreement with molecular dynamics simulation of MoS_2 nanotubes. The nanotubes were deformed elastically until failure, in "sword in a sheath" mechanism and probably fractured in a brittle mode.

Clamped nanotubes were bent and the shear (sliding) modulus was obtained according to Timoshenko's bending equation and found to be 2GPa. This value is in good agreement with DFTB calculations (4GPa) for sliding of two adjacent layers of MoS_2.

Furthermore, a unique nonlinear elastic deformation was observed both in post buckling and in bending tests. This mode of deformation is associated with the tubular structure.

5:20pm **TR+SS-TuA11 Nanotribological Characterization of Various Skin Cream Ingredients using Atomic Force Microscopy**, ***W. Tang***, *B. Bhushan,* The Ohio State University, *S. Ge*, China University of Mining and Technology

Skin cream is used to improve skin health and create a smooth, soft, pliable, and moist perception by altering the surface friction, adhesion, elastic modulus, and surface potential of the skin surface. As the industry continually searches for better cream formulations, it becomes increasing necessary to study how different cream ingredients interact with skin surface on the nanoscale. In this paper, vaseline, glycerin, and lanolin oil, which are the widely used ingredients in moisture cream, as well as the common moisture cream, advanced moisture cream, and oil-free moisture cream, were studied using an atomic force microscope (AFM). The binding interaction between skin cream and skin surface is one of the important factors in determining cream thickness and consequently the proper performance of skin cream. Film thickness, adhesive force and effective Young's modulus of various cream treated skin was measured using the force calibration plot technique with the AFM. Skin goes through various daily activities with time and the durability properties are closely tied to product performance. The durability of various skin creams were studied by repeated cycling tests. The health and feel of skin are significantly affected by its surface charging and the surface potential of virgin skin, and various cream treated skin was measured to determine the effects of various skin cream using the Kelvin probe method with the AFM. Relevant mechanisms are discussed.

5:40pm **TR+SS-TuA12 An Imaging TOF-SIMS Study of the Tribochemical Interactions in Diamondlike Carbon Films**, ***A. Erdemir***, *O. Eryilmaz*, Argonne National Laboratory

Diamondlike carbon (DLC) films combine many attractive properties which make them good prospect for a wide range of engineering applications. Depending on the sources of carbon (i.e., hydrocarbon gases or solid carbon or graphite targets) and the type of deposition method, some of the DLC films may contain large amounts of hydrogen in their structures and they are relatively soft. Those that are produced from solid carbon and/or graphite targets by arc-PVD and pulsed laser deposition are nearly hydrogen free but very hard. However, regardless of their chemical and/or structural nature, all DLC films tend to be very sensitive toward the chemical composition of the test environments when tested for their friction and wear properties. In this study, we concentrate our attention on the friction and wear behaviors of both the hydrogenated and hydrogen-free DLC films in the presence of inert and reactive gaseous species like, argon, oxygen, hydrogen, and deuterium in test chambers. Using time-of-flight secondary electron mass spectrometry (TOF-SIMS), we explore the extent of tribochemical interactions that occurred during sliding tests. These studies have confirmed that the friction and wear behaviors of DLC films are indeed very closely controlled by the type and extent of tribochemical events that are triggered by the gaseous species in the surrounding atmosphere. In particular, hydrogen and deuterium in test environments seems to interact with the sliding surfaces of these films and thus have the greatest effect on friction and wear. Inert gases were detrimental for the friction and wear behaviors of hydrogen-free DLC, but beneficial to that of the highly hydrogenated DLC films. Based on the results from TOF-SIMS studies, we provide a mechanistic explanation for the tribochemistry of sliding surfaces and correlate these findings with the friction and wear behaviors of DLC films.

Tribology Focus Topic
Room: C4 - Session TR+NS-WeM

Nanomechanics and Nanotribology

Moderator: C.M. Mate, Hitachi San Jose Research Center

8:00am **TR+NS-WeM1 Nonlinear Contact Area Dependence of Sliding Friction for Metallic Nanoparticles**, ***D. Dietzel***, *T. Moenninghoff, A. Schirmeisen*, University of Münster, Germany

The existence of superlow friction under appropriate interface conditions is one of the most intriguing concepts in nanotribology. If an interface between two incommensurate surfaces is atomically clean, a state of virtually frictionless sliding is anticipated, often referred to as 'superlubricity' or 'structural lubricity'. But although superlubricity is a widely accepted theoretical concept, an unambiguous and direct verification has been difficult in the past. Theory predicts that the lattice mismatch at the interface causes a decrease of the potential barrier between stable states with increasing contact size that ultimately leads to vanishing friction. Therefore, analyzing the contact area dependence of superlubric friction might be a straightforward approach to confirm the frictional conditions.

Unfortunately, conventional friction force microscopy (FFM) has limitations inherent to the experimental configuration when it comes to contact area dependent measurements: Apart from the rather limited variety of material combinations, the fixed tip radius makes it especially difficult to analyze effects as a function of the contact area. In order to analyze the contact area dependence of interfacial friction, the friction between two objects in relative motion with a well-defined contact area should be measured instead of the friction between tip and surface. Therefore we have manipulated nanometer scale metallic particles on atomically flat surfaces by contact mode atomic force microscopy techniques and quantitative information on interfacial friction has been extracted from the lateral manipulation of these nanoparticles[1]. In previous experiments[2] we found two distinct frictional states during particle sliding of Sb-particles on HOPG substrate: Some particles show finite friction increasing linearly with interface area, thus reinforcing Amonton's law at the nanoscale, other particles assume a state of frictionless or 'superlubric' sliding.

In this contribution we show new measurements which were concentrated on the particles exhibiting vanishing friction. By optimizing our experimental sensitivity we succeeded for the first time to analyze the contact area dependence of friction force of these low friction particles. In contrast to the 'Amonton'-like particles, interfacial friction of the low friction particles showed strongly nonlinear contact area dependence. The experimental results are compared to theoretical considerations, which predict that the shear stress of sliding superlubric particles should decrease with increasing particle size.

[1]Dietzel et al., J. Appl. Phys.102, 084306 (2007).

[2]Dietzel et al., Phys. Rev. Lett. 101, 125505 (2008).

8:20am **TR+NS-WeM2 Why is Graphite so Slippery? Gathering Clues from Atomically Resolved Three-Dimensional Lateral Force Measurements**, ***M.Z. Baykara***, *T.C. Schwendemann, B.J. Albers, N. Pilet, E.I. Altman, U.D. Schwarz*, Yale University

Conventional lateral force experiments give insufficient insight into the fundamental reasons for graphite's outstanding qualities as a solid lubricant due to an averaging effect caused by the finite contact area of the tip with the sample. To overcome this limitation, we used a noncontact atomic force microscopy-based approach that enables use of atomically sharp tips. The new technique [1], performed using a home-built low temperature, ultrahigh vacuum atomic force microscope [2], allows the measurement of normal and lateral surface forces in a dense three-dimensional raster with picometer and piconewton resolution.

In this presentation, we analyze the height and lattice site dependence of lateral forces, their dependence on normal load, and the effect of tip shape in detail. The lateral forces are found to be heavily concentrated in the hollow sites of the graphite lattice, surrounded by a *matrix* of vanishingly small lateral forces. It will be argued that this astonishing localization may be a reason for graphite's excellent lubrication properties. In addition, the distance and load dependence of the lateral forces experienced along possible "escape routes" from the hollow sites, which would be followed by a slider that is dragged out of them, are studied. Surprisingly, the maximum lateral forces along these escape routes, which ultimately determine the static friction, are found to depend linearly on normal load, suggesting the validity of Amontons' law in the noncontact regime.

[1] B. J. Albers *et al.*, Nature Nanotechnology **4**, 307 (2009).

[2] B. J. Albers *et al.*, Rev. Sci Instrum. **79**, 033704 (2008).

8:40am **TR+NS-WeM3 Atomistic Simulations of Friction and Wear of Carbon-Based Materials**, ***I. Szlufarska***, *Y. Mo, M. Mishra*, University of Wisconsin, Madison **INVITED**

Controlling tribological properties requires understanding a bewildering array of interrelated mechanisms, including elastic instabilities, plastic deformation, fracture, and chemical reactions. Large scale atomistic simulations have been used to unravel some of these mechanisms. Tribological studies are typically divided into a wearless regime, where deformation is primarily elastic, and a wear regime where permanent deformation occurs. For wearless contacts, I will discuss the breakdown of continuum mechanics at the nanoscale and present our recent discovery of friction laws in dry nanoscale contacts. This discovery lays a foundation for unified friction laws across all length scales. In the wear regime I will focus on the origins of recently observed ductile wear in nominally brittle SiC. Although this ductile wear holds potential for greatly enhancing the ease of machining of high-performance ceramics, its origin is still an open question. I will evaluate potential mechanisms for ductile wear, including the possibility of transformation to more ductile phases, dislocation mediated plasticity, and nanoindentation-induced amorphization.

9:20am **TR+NS-WeM5 MD and AFM Studies of the Adhesion of Diamond, Silicon, and UNCD**, ***J.A. Harrison***, *P.L. Piotrowski, G.T. Gao,* United States Naval Academy, *R.J. Cannara,* National Institute of Standards and Technology, *R.W. Carpick*, University of Pennsylvania

For the past several years, we have used molecular dynamics (MD) simulations and classical reactive empirical bond-order (REBO and AIREBO) potentials to elucidate the atomic-scale mechanisms of friction and adhesion in solid lubricants. Recently, we have conducted complementary MD and atomic force microscopy (AFM) examinations of adhesion and atomic-scale friction for diamond, silicon, and nanocrystalline diamond interfaces. These materials are highly relevant to micro- and nano-electromechanical systems (M/NEMS), nanomanufacturing, and a host of other applications. The conditions of the simulations and the experiments were designed to correspond as closely as the methods allow. The effects of variables including diamond (or silicon) crystal orientation, hydrogen termination, temperature, and roughness on adhesion and friction can all be examined. In this talk, we will discuss our most recent results which highlight atomic mechanisms of friction and adhesion as well as the limits of continuum mechanics.

*JAH acknowledges support from The Air Force Office of Scientific Research (AFSOR) as part of the Extreme Friction MURI and from The Office of Naval Research. JAH & RWC also acknowledge support from AFOSR's Aerospace, Chemical, and Material Sciences Directorate.

9:40am **TR+NS-WeM6 Which Fractal Parameter Most Determines Adhesion?**, *D. Liu,* Worcester Polytechnic Institute, *J. Martin,* Analog Devices, Inc., ***N.A. Burnham***, Worcester Polytechnic Institute

The topography of a surface can be characterized by three fractal parameters: its surface roughness, its roughness exponent, and its lateral correlation length [1]. In 2001, T.S. Chow [2] predicted that a decrease in adhesion by orders of magnitude would follow from increasing the roughness exponent of a surface (i.e. by making it smoother), and that adhesion could also be lowered by decreasing its lateral correlation length (shorter wavelength). In 2007 [3], we published a simple analytical model, together with experimental data, that demonstrated the strong influence of surface roughness on adhesion. This year, using atomic force microscopy, experimental data were collected from MEMS sidewalls of varying topography but with the same chemical treatment in order to untangle which of the three fractal parameters is – or are – most important in determining adhesion. The data are inconsistent with Chow's predictions; his assumption was that only the asperities on the surface contribute to the adhesion. In contrast, our numerical simulations of the tip-sample adhesion for surfaces with varying fractal parameters include both the asperities and the bulk of the sample.

Together with the simulations, the previous and current experimental data support the conclusion that surface roughness is a significant predictor of adhesion, with the adhesion dropping by more than an order of magnitude for a roughness change from 1 to 10 nm. For the roughness exponent, the simulations follow the same trend as Chow's predictions, in that adhesion should decrease with increasing roughness exponent (smoother), but rather than predicting orders of magnitude change, the simulations reveal only a 20% decrease as the roughness exponent changes from 0 to 1. Here, the experimental data were more consistent with the simulation than Chow's predictions, although they were not conclusive. The scatter in the data was

large, and the range of the roughness exponent only varied from 0.85 to 0.99, for which the simulations predict a change in adhesion of approximately 10%. For the lateral correlation length, the experiment showed a wide range of adhesion values for smaller correlation lengths and low adhesion for larger correlation lengths (longer wavelengths); we are still investigating the theoretical basis of this observation. We hope to contribute to the understanding of adhesion so as to minimize stiction in MEMS.

References

1. A.-L. Barabasi and H.E. Stanley, Fractal concepts in surface growth (1995)

2. T.S. Chow, Phys. Rev. Lett. 86, 4592 (2001)

3. D. Liu, J. Martin, and N.A. Burnham, Appl. Phys. Lett. 91 043107 (2007)

10:40am **TR+NS-WeM9 Multiscale Modelling of the Indentation and Scratch Damage of Ultrathin Coatings on Architectural Glass**, ***S.J. Bull***, *A. Oila*, Newcastle University, UK

Although optical coatings are generally designed for their functional requirements it is often the mechanical properties of the system which limits performance. For instance, the major in-service failure mechanism of modern solar control coatings for architectural glass can be scratch damage. Many of these coatings are multilayer structures made from individual layers of less than 100nm thickness and different coating architectures are possible (i.e. different layer materials, thicknesses and stacking order). To assess their mechanical response, coated samples may be subjected to indentation and scratch tests; however, it is not always possible to predict the failure mechanisms of such coatings and modelling approaches have to be developed to understand the deformation mechanisms. This presentation will focus on the problems of measuring the plasticity and fracture properties of very thin coatings (<100nm) and the use of multi-scale modelling approaches to predict performance for coatings on glass.

11:00am **TR+NS-WeM10 Cognitive Molecular Engineering In Nanotribology - Intrinsic Friction Analysis**, *D.B. Knorr*, ***R.M. Overney***, University of Washington

In the new *Age of Molecular Engineering*, one of the objectives is to cognitively design molecules that if condensed, provide materials with anticipated properties. In regards of tribological systems, such as lubricants, the objective would be to offer chemists with molecular design parameters based on which molecules could be synthesized that dissipate energy in a targeted fashion. Thereby, the input would come either directly from experimental observations, or indirectly via computer simulations that are based on models that are relevant to the materials.

This is in contrast to the majority of current research efforts in tribology or nanotribology. State-of-the-art molecular models in tribology focus on generic periodic potentials that are thermally and mechanically inert. Experimental methods provide mostly only phenomenological parameters, such as the friction coefficient, or process descriptive parameters, such as the stick-slip phenomena. Such generic “black-box” approaches, fail to address frictional energy dissipation that are linked to material intrinsic molecular or submolecular modes of relaxation, and hence, do not provide the necessary input for a cognitive molecular design strategy for an effective tribological system.

This talk will highlight the importance of material intrinsic relaxation modes for frictional dissipation involving organic systems. Phenomenological friction analysis data, i.e., friction coefficients from friction-load curves, will be contrasted with spectroscopic data from an intrinsic friction analysis (IFA), involving a time-temperature superposition analysis of friction-velocity isotherms. Both data analysis methodologies, involving lateral force microscopy, reveal an astonishing correspondence regarding the dissipated energy and the energy involved in activating intrinsic relaxation modes and cooperative phenomena. Specifically, we will address surface and sub-surface energy relaxations in amorphous macromolecular model system (e.g., polystyrene) and their relevance to frictional energy dissipation within well defined loading regimes. Depending on the coupling strength (cause for cooperativity) between molecular actuators involved (e.g., rotating side chains or translating polymer backbones) the dissipation in energy can carry a significant entropic energy contribution, accounting for up to 80% of the apparent Arrhenius activation energy. The IFA methodology discussed in this paper that provides direct insight into the enthalpic and entropic energy contributions of friction dissipation processes is shown to be well suited as an analysis tool towards cognitive molecular engineering in tribology.

11:20am **TR+NS-WeM11 Optimization of Tailored Multifunctional Nanocomposite Structures**, ***T. Shenk***, *R. Winter*, *K. Benjamin*, South Dakota School of Mines and Technology

Polymer nanocomposites provide unique solutions to industrial and scientific applications where weight must be minimized and functionality maximized. Researchers are interested in improving the ability to tailor a product to meet specific weight, thermal, optical, mechanical and electrical requirements. Historically functional composite structures have been realized through a top-down approach. With the advent of atomic level measurement tools and experimental techniques a bottom-up approach to the creation of multifunctional structures is receiving intense study. We are developing unique multifunctional structures using such a bottom-up approach with the intent of developing molecular simulations to guide such a process. Properties of polymeric nanocomposite structures are tailored and optimized through a fundamental understanding of intermolecular forces. While macroscopic models of bulk properties of polymer nanocomposites have been characterized, much less is known on the dynamics of their interfacial characteristics, which must be fully developed in order to be able to tailor fabrication of multifunctional nanocomposites using the bottom-up approach. Self assembly, targeted functionalization and spin coating are used to provide consistent means of creating multilayer multifunctional thin film composite strictires allowing for the investigation of multifunctional composites. We investigate the affects of sonication, high shear mixing, and surface modification on the ability to control dispersion to create and predict multifunctional layers of epoxy spin coated nanocomposites and control desired mechanical properties such as conductivity, optical transmission and absorption, loss and storage moduli and coefficient of thermal expansion. The Interfacial Force Microscope (IFM), coupled with the Biaxial Loading Instrument, which allows for refined and uncoupled control of mixed-mode characterization of interface adhesion, will be used to determine interfacial characteristics of these multi-functional composites.

Tribology Focus Topic
Room: C4 - Session TR+SE-WeA

Advances in Surface Engineering for Friction and Wear Control

Moderator: S.S. Perry, University of Florida

2:00pm **TR+SE-WeA1 The Deposition of Highly Adherent Fullerene-Like CN_X Coatings on Steel Substrates of Complex Geometry**, ***E. Broitman***, Linköping University, Sweden & Carnegie Mellon University, *S. Schmidt, G. Greczynski*, Linköping University, Sweden, *Zs. Czigany*, Research Institute for Technical Physics and Materials Science, Hungary, *C. Schiffers*, CemeCon AG, Germany, *L. Hultman*, Linköping University, Sweden

Due to their superior wear resistance, high hardness, and low friction coefficient, carbon nitride (CN_x) coatings have been proposed as a candidate to replace diamond-like carbon (DLC) coatings. In this study we present the structural, morphological, and adhesive properties of fullerene-like (FL) and amorphous carbon nitride (CN_x) coatings synthesized by HIPIMS in an industrial CC-800/9 CemeCon equipment. The coatings were grown on steel substrates of complex geometry (including those with small diameter cavities and holes, and shapes such as bolts, nuts, and screws) to thickness of 2-3 µm. A novel HIPIMS pretreatment with two HIPIMS power supplies was used to increase the adhesion of the coatings: one power supply to establish the discharge and one to produce a pulsed substrate bias. The environment of the created Cr plasma sputter-cleans the surface and forms a Cr-containing gradual interface into the substrate. Subsequently, carbon nitride coatings were prepared by HIPIMS from a high purity graphite target in a N_2/Ar discharge at 3 mTorr with the N_2 fraction varied from 0 to 1, and the substrate temperature varied from ambient to 300 °C. X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), scanning transmission microscopy (STEM), and high resolution transmission electron microscopy (HRTEM) have been used to study the coating and the steel/Cr/CN_x interfaces. Identification of coating adhesion failures was done by the Daimler-Benz Rockwell-C adhesion test.

2:20pm **TR+SE-WeA2 Tribological and Mechanical Properties of Nanostructured Hydrogenated Amorphous Carbon and TiB2 Films**, ***B. Zhao***, *Y.W. Chung*, Northwestern University

Hydrogenated amorphous carbon films (CHx) are known to attain ultra-low friction performance only in dry environments. Our work demonstrated that sulfur doping of hydrogenated carbon films (CHx+S) 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 nanostructured coatings is known to improve hardness. With the aim to produce hard, low-friction coatings, we synthesized nanostructured films of CHx (or CHx+S) and titanium diboride using dual-target magnetron sputtering. Titanium diboride deposited by this method had a hardness >30 GPa. This paper will discuss the film structure as well as tribological and mechanical properties. Nanolayered films with a majority titanium diboride composition showed hardness improvement around rule-of-mixtures values with favorable low friction performance in humid air.

2:40pm **TR+SE-WeA3 Tribological Characteristics of a Tungsten Tip/ Au-Ni Alloy Interface, Studied by Means of Combined STM-QCM**, ***L. Pan***, *J. Krim*, North Carolina State University

A two-phase Au-Ni (20 at.% Ni) alloy has recently been suggested as a potential contact material for RF switch microelectromechanical systems (MEMS) switches. Tribological properties impact switch closure behaviour and heating at the interface impacts both the electrical and mechanical properties of the switch. We have thus performed a QCM STM study of heating and wear at the interface between a tungsten tip and a range of gold nickel alloys with varying compositional percentages.The comparison of nano heating generated via friction and surface response to the tip crash would be shown here.

3:00pm **TR+SE-WeA4 Quantitative Measurements of Adhesion Forces in Polycrystalline Silicon Surfaces via a Doubly Clamped Beam Test Structure**, ***I. Laboriante***, *B. Bush, G. Li, C. Carraro, R. Maboudian*, University of California - Berkeley

Current state of knowledge indicates that the prevalence of static adhesion in microstructures remains one of the major hurdles preventing a larger number of MEMS-based products from entering the mainstream, and quantitative understanding of this phenomenon is currently lacking. This is due to the fact that contact mechanics at the micro-/nanoscale are a complicated multiscale problem, in particular when one is dealing with rough and rigid impacting surfaces. The results of investigations aimed at elucidating the adhesion force between co-planar, impacting polycrystalline silicon surfaces will be presented using a microfabricated doubly clamped cantilever beam test structure. The effect of apparent area of contact will be examined via microfabricated dimples of varying size. Determination of adhesion forces through systematic optical interferometric measurements will be presented. The data reveal a weak dependence of adhesion on the apparent contact area, instead of scaling with the contact area. Possible mechanisms leading to this behavior will be discussed.

4:00pm **TR+SE-WeA7 Nanoscale Control and Understanding of Friction at High-Speeds for Future Disk Drive Head-Disk Interfaces**, ***C.M. Mate***, Hitachi San Jose Research Center **INVITED**

Tremendous progress has been made over the past several decades towards understanding the nanoscale origins of tribological phenomena [1], leading to numerous breakthroughs in friction and wear control. The impact of these breakthroughs has been particularly striking in the disk drive industry, where improved tribological engineering of the head-disk interface has led to the magnetic spacing being reduced from ~100 nm in 1995 to ~10 nm in 2009, enabling a 10^3 increase in storage areal density. In today's drives, recording head sliders fly reliably at incredibly small clearances (~2 nm during read-write operations) for many years at speeds > 10 m/s. As the industry moves to even smaller spacings, however, head-disk contact will become more frequent and improved surface engineering to control friction and wear will become more paramount.

In this talk, I will first review the key surface engineering features (slider air bearing surface, disk topography, overcoat, lubricant, etc.) that enable today's disk drive sliders to fly at nanometer clearances over disk surfaces. I will then describe work going on in our laboratory both to determine the nanoscale origins of friction and to use this understanding to develop future head-disk interfaces that are expected to run in continuous contact.

To determine the nanoscale origins of friction at high-speed sliding contacts (> 1 m/s), we have developed a *high shear rate apparatus* using technology from the disk drive industry [2]. With this new instrument, friction, adhesion, and wear can be studied at high sliding speeds (1 to 100 m/s) for nanometer thick lubricant films sandwiched between atomically smooth surfaces. Recently, this instrument has been modified to incorporate optical microscopy for in-situ visualization when a slider runs in contact with a transparent rotating disk. This technique has been particularly useful for studying the formation of nanoscale, non-equilibrium menisci at high speed contacts.

[1] C.M. Mate, Tribology on the Small Scale: A Bottom up Approach to Friction, Lubrication, and Wear, Oxford University Press, Oxford, 2008.

[2] C. M. Mate, R.N. Payne, Q. Dai, K. Ono, *Phys. Rev. Lett.* 97 (2006) 216104.

4:40pm **TR+SE-WeA9 The Effects of Humidity on the Tribological Properties of Nanocrystalline Diamond**, ***N. Theodore***, *K.J. Wahl*, Naval Research Laboratory

The tribological response of nanocrystalline diamond (NCD) coatings to variations in moisture content of the environment was examined under reciprocating sliding conditions. Surface roughness, structure, composition, and carbon chemistry were determined by atomic force microscopy (AFM), X-ray diffraction (XRD), and Raman spectroscopy. All coatings were nanocrystalline with crystallite sizes ranging from to 4 to 60 nm as measured by XRD. Visible wavelength Raman spectroscopy of the NCD coatings revealed various carbon chemistries. The NCD coatings could be classified in three subsets by Raman microscopy: (1) coatings exhibiting a single strong peak at 1332 cm^{-1} typical of crystalline diamond bonding; (2) coatings possessing broad peaks at 1340 cm^{-1} and 1550 cm^{-1} characteristic of the *D* and *G* peaks in sp^2 hybridized carbon along with the diamond 1332 cm^{-1} peak; and (3) coatings displaying additional peaks at 1135 cm^{-1} and 1470 cm^{-1}, commonly attributed to trans-polyacetylene bonding, along with the three previously described peaks. Reciprocating sliding tests using sapphire counterfaces in controlled humid environments resulted in low friction values for all coatings, between 0.02 and 0.09. Decreasing the humidity caused an increase in the number of cycles to run-in to low friction. These observed differences in run-in and counterface wear as a function of environment will be presented and related to NCD coating composition and microstructure.

5:00pm **TR+SE-WeA10 Crystallography-Dependent Self-Lubrication on Nickel Surfaces During Wear**, ***C.C. Battaile***, *S.V. Prasad, J.R. Michael, P.G. Kotula*, Sandia National Laboratories

Wear experiments on Ni surfaces show that stable, nanocrystalline tribofilms can form under appropriate tribological conditions, even on single crystals. The presence of these nanocrystalline layers is qualitatively dependent on the crystallography of the surface and wear orientations, and are responsible for a marked reduction in friction on bare contact, suggesting numerous surface engineering possibilities. For example, when a 1 N normal load and 3.75 mm/s tangential speed are applied to a 1/8" diameter Si3N4 ball in contact with electropolished single-crystal Ni in a dry nitrogen environment, the measured friction coefficient is usually in the range 0.6 to 0.8. However, when the Ni surface is of the {110} type and the sliding direction is <211>, the friction coefficient abruptly drops to 0.3 after about 500 cycles, where it remains indefinitely. Modeling of this phenomenon, based on crystal plasticity, microstructure formation, and grain boundary sliding, suggests that the self-lubrication is due to the capacity of ultra-fine-grained microstructures to support grain rotation. Wear experiments on bulk nanocrystalline Ni deposits support this hypothesis by demonstrating low friction coefficients (around 0.3) and virtually no wear-in under low loads and sliding speeds, and higher friction (around 0.6) under high loads and speeds. We will provide an overview of the experiments and modeling of nanocrystalline film formation on single-crystal Ni, detail the results from friction experiments on bulk nanocrystalline Ni, and discuss model validation of the phenomenon's strain rate sensitivity.

5:20pm **TR+SE-WeA11 NEXAFS Characterization of Vapor Deposited Monolayer and Submonolayer Films on Si and Al_2O_3 for MEMS Friction Control**, ***C. Jaye***, *D.A. Fischer*, National Institute of Standards and Technology, *B.M. DeKoven*, Surface and Interface Consulting, *J.D. Chinn*, Integrated Surface Technologies

Most microelectromechanical systems (MEMS) are fabricated using semiconductor and ceramic materials such as Si, and SiO2, and Al2O3 which are hard, brittle materials and are not commonly used for mechanical devices. MEMS components are very small and lack power or much inertia when in motion, so they are highly susceptible to the influence of adhesive and surface forces. MEMS lubrication schemes involving vapor phase lubrication have been proposed as a means of continuously replenishing lubricant films on MEMS surfaces.

We present synchrotron based near edge x-ray absorption fine structure (NEXAFS) spectroscopy results of vapor deposited monolayers and submonolayers on SiO2 and Al2O3 substrates under different process conditions. NEXAFS is a powerful non-destructive method in which soft x-rays are absorbed followed by the excitation (transition) of electrons from a core K- or L-level to partially filled into empty low-lying antibonding molecular states. Bond orientation information is deduced from the changes in the intensity of the resonances upon rotating the substrate normal in the plane of incidence of the polarized synchrotron beam.

Carbon K-shell NEXAFS performed at different incidence angles revealed that the vapor deposited fluorodecyltrichlorosilane (FDTS) molecules on silicon and alumina substrates produced self-assembled monolayered films that have high surface coverage and can be highly oriented. Using the NEXAFS technique, dichroic ratios (based on the **σ*C-F** resonance) of the order of 0.5 have been obtained, thus revealing that these FDTS films have a high degree of molecular orientation. Orientation and coverage comparisons for water wiped and isopropylalcohol wiped FDTS as well as directly vapor deposited FDTS will be presented. The implications for the design of surfaces and interfaces for stiction control in MEMS devices will also be discussed.

Tribology Focus Topic
Room: Hall 3 - Session TR-ThP

Tribology Poster Session

TR-ThP1 XPS Study of Ti Surface Reactivity under Friction in Various Nitrogen Environments, ***T. Le-Mogne***, *C. Mary*, *J.M. Martin*, Ecole Centrale de Lyon, France

Thanks to their high strength to weight ratio and good corrosion resistance, Ti alloys are widely used for various industrial applications and may be exposed to several environmental conditions. In a previous study, the authors have pointed out the evidence of titanium tribochemical reaction with nitrogen under fretting in air.

In order to investigate this phenomenon and especially the effect of friction on the nitriding mechanisms of Ti alloys, an experimental simulation was conducted in a specific Environment-Controlled Tribometer (ECT) coupled with in-situ X-ray Photo-electron Spectroscopy (XPS) analysis. Several Ti/Ti reciprocating sliding tests were performed with a pin on flat geometry successively in high vacuum, in N_2 environment and in air. The objectives were to investigate the reactivity of Ti surfaces with nitrogen in several tribological situations: after removal of native oxide layer by Ar+ etching, after friction under vacuum followed by N_2 exposure and after friction under N_2 environment. This approach proposes conditions needed for Titanium reaction with nitrogen.

TR-ThP2 Friction and Sliding Wear Behavior of nc-TiN/a-Si_3N_4 Nanostructured Coatings, ***J. Garcia***, *M. Flores*, Universidad de Guadalajara, Mexico

The present work is related to the evaluation of dry sliding wear resistance of a sputtered PVD nanostructured nc-TiN/a-Si_3N_4 coating, deposited on Stainless steel 316L substrates. X-ray diffraction is used to analyze the nanostructure of the film. The topography of substrates, films and Wore Surfaces were analyzed by profilometry. Film adhesion to the substrate was evaluated by scratch-tests. The surface hardness was measured with a Vickers micro-hardness tester. The wear resistance was evaluated by Pin-on disk under a normal load in the range of 2 to 10 N and a constant tangential speed of 0.15 m/s and reciprocating apparatus with a frequency of 1 Hz and a normal load within the same range established above, both tests in dry conditions. After these tests, on the coating as well as on the counterpart, the wear mechanisms developed were analyzed by Optical Microscopy, the wear tracks were measured and the wear rate was calculated and discussed.

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