# Friday Morning, November 14, 2014

## Tribology Focus Topic
## Room: 303 - Session TR-FrM

### Applications of Novel Materials in Tribology
**Moderator:** BarbaraL Mooney, United States Naval Academy

8:20am **TR-FrM1 Direct Adhesion between Stiff Materials: Characterization and Applications in Nanomanufacturing**, ***Kevin Turner***, University of Pennsylvania **INVITED**

Micro- and nano-scale contacts that adhere directly due to surface forces are ubiquitous in semiconductor bonding and stacking processes as well as in AFM-based nanolithography. Understanding and characterizing the mechanics of direct adhesion in these processes is essential to advancing process capability. This presentation will discuss two different studies in which the adhesion of small-scale contacts in micro- and nanosystems were examined. First, a study of the direct adhesion of single crystal silicon components will be discussed. A microbeam-based method was used to characterize adhesion hysteresis of smooth single crystal silicon contacts in varying levels of relative humidity. The results show significant hysteresis between adhesion and separation and have implications for processes such as direct wafer bonding and nanomembrane stacking via microtransfer printing. Second, a study of the role of geometry on the adhesion of single asperity nanoscale contacts, such as those formed by an AFM tip in contact with a surface, will be discussed. Specifically, the effect of deviations in the tip geometry from the ideal parabolic geometry assumed in the classical models (e.g., JKR, DMT) was examined. A combination of analytical modeling, finite element simulations, and experiments were used to quantify the effect of changes in tip geometry on the relationship between pull-off force and work of adhesion. Furthermore, the role of roughness on the effective adhesion range is examined. The implications of both of these studies on nanomanufacturing processes will be discussed.

9:00am **TR-FrM3 Compound, Nanometric Cushion for Enhancing Tribological Characteristics of Hard Films**, *K. Gotlib-Vainshtein, O. Girshevitz, C.N. Sukenik*, Bar Ilan University, Israel, *D. Barlam*, Ben Gurion University, Israel, ***Sidney Cohen***, Weizmann Institute of Science, Israel

In this work, scanning force microscopy (SFM) is used to measure tribological characteristics of a novel, compound film. Hard coatings are often applied to engineering surfaces for reduction of friction and wear. Here, we show that a soft, flexible, intermediate layer placed between substrate and hard outer coating provides considerable enhancement of the wear protection. Previously, we demonstrated that such compound films provide a means to controllably tune surface stiffness, thus opening interesting nanomechanical applications.[1] Titania films of several nm thickness are coated onto substrates of silicon, kapton, polycarbonate (PC), and polydimethylsiloxane (PDMS) and the scratch resistance is measured by SFM. When PDMS is applied as an intermediate layer between any stiffer substrate and the thin titania outer layer, marked improvement in the scratch resistance is achieved. This is shown by quantitative wear tests on silicon and kapton substrates coated with PDMS which is subsequently capped by a titania layer with thickness ranging from several nm to several tens of nm. In addition to the improvement in scratch/wear resistance, nano-friction studies performed in the SFM showed that the PDMS cushion layer reduced the friction coefficient of the titania coating by more than a factor of two.

To demonstrate a technological application of such coatings, they were applied to the common lens material PC. Here, 40 nm or titania was deposited by liquid phase deposition[2] on a ten micrometer-thick PDMS “cushion” on top of the PC. In scratch tests, load to failure was increased by 5x relative to untreated PC and more than doubled relative to titania on PC without the cushion layer. These thin coatings had no detrimental effect on the optical properties of the PC. This work thus demonstrates, a simple, robust, and practical means of improving tribological properties in practical applications.

The physical basis of this effect is explored by means of Finite Element Analysis, and we suggest a model for friction reduction based on the "cushioning effect” of a soft intermediate layer.

9:20am **TR-FrM4 Friction Effects by Surface Roughness and Sliding Speeds at Oil Lubricating Conditions**, ***Guang Wang***, *X. Nie,* University of Windsor, Canada, *J. Tjong*, Ford Motor Company, Canada

A linerless aluminum (Al) engine block has potential in reducing the weight of an automotive engine for improvement of the fuel economy. However, the Al cylinder surface of an aluminum engine block is not usually strong enough to withstand the sliding wear against piston rings. A few surface processing technologies are used to protect the surface of cylinders directly. Among them, plasma transferred wire arc (PTWA) thermal spraying coating is already popular. Plasma electrolytic oxidation (PEO) coating is also proposed for increasing the wear resistance of aluminum-silicon alloy (A356) and reducing the friction between the cylinder and piston. In this work, two different PEO coatings with a thickness of around 25mm were prepared, and a high speed pin-on-disc tribometer was used to study the tribological behavior of the coating at oil lubricant conditions. A cast iron sample was also used to do the same tribological tests for comparison. The coefficient of friction (COF) vs surface roughness (Ra: 0.2-0.8μm) and sliding speeds (up to 6.0m/s) were particularly studied. The results show that the COF significantly decreased with the increase of sliding speeds, and a smoother coating surface generally exhibited a lower COF. The roughness also influenced the descent rate of the COF significantly. The COF of the PEO coatings could be lower than that of cast iron. The study indicates that the Al-Si alloy with PEO coatings could be a feasible solution to reduce weight and improve fuel efficiency of an Al engine.

9:40am **TR-FrM5 Basal Plane Surface Functionalization of Graphene Nanoplatelets**, ***J. David Schall***, Oakland University

Due to their high in-plane strength, electrical and thermal conductivity and lubricity, graphene nanoplatelets (GnP) have great potential in polymer composite and lubricant additive applications. However, to fully utilize these remarkable properties the GnPs must be functionalized in such a way as to make them attractive to the matrix in which they are embedded. Traditionally GnPs are functionalized via wet chemical methods along their edges. Because of the high surface to edge ratio, the benefits of this functionalization are limited and unfortunately functionalization of the basal plane tends to lead to degradation of the beneficial properties. Graphite-like molecules such as Pyrene have been proposed as an alternative way to increase GnP-matrix interactions. Pyrene, which can be thought of as a small graphene sheet consisting of only four rings, interacts with the surface of the GnP via dispersion forces as opposed to chemical bonding. The pyrene itself is functionalized with alkane chains or carboxylic acid groups which then interact with the surrounding matrix material. In this paper, results from molecular simulations of the interactions between functionalized pyrene molecules and graphene nanoplatelets will be presented. These simulations have been used to measure the interaction strength between GnPs and functionalized pyrene as well as to investigate the effect of the functionalized chain length on the interaction with a poly-alpha olefin based lubricant. The aim of this work is to explore mechanisms to improve stability of GnPs in lubricants such as engine oil which is dependent upon strong interactions between the GnP and the liquid matrix to prevent settling.

10:00am **TR-FrM6 Nanoscale Wear of Patterned PMMA Structures**, ***Yijie Jiang***, *Z.B. Milne*, University of Pennsylvania, *M. Fallet*, *J.A. Harrison*, United States Naval Academy, *R.W. Carpick*, *K.T. Turner*, University of Pennsylvania

Atomic force microscopy (AFM) is increasingly used for probe-based metrology and tip-based nanomanufacturing (TBN) processes. In these processes, a sharp silicon- or carbon-based tip often interacts with the surface of a polymer film on a substrate. During this mechanical interaction, the polymer film can wear and contaminate the tip. To improve the reliability and control of these processes, a fundamental understanding of the tribological properties of nanoscale tip-polymer contacts is required.

Polymethyl methacrylate (PMMA), a common polymer used in nanofabrication, is studied here. PMMA is used as a resist in electron-beam (e-beam) lithography and also employed in TBN processes to realize 2D patterns and 3D structures. The tribological properties of PMMA are important in the optimization and selection of operating parameters in TBN processes and AFM-based metrology. Studies of PMMA wear have been performed from the millimeter- to nano-scale. The reported wear rates of PMMA vary over a wide range, likely due to differences in PMMA compositions tested, varied experimental conditions, and lack of control for the effect of debris. The debris can contaminate both the surface and the tip, and this often makes it difficult to accurately assess wear in experiments at the small scale.

In this work, nanoscale wear of PMMA is investigated using systematic AFM-based nanomechanical wear experiments. The experiments are performed on thin PMMA layers (131±4 nm thick) on silicon substrates. To allow for precise quantification of the evolution of the PMMA, the film is patterned via e-beam lithography into structured patterns. The gaps between the patterns minimize debris and also facilitate tip cleaning. The structures primarily consist of long rectangular and square structures of PMMA. The exposed Si surface in the gaps serves as a reference surface, which allows for accurate measurements of film height to be obtained throughout the test. The use of AFM for applying the mechanical load and scanning as well as for imaging the structures allows for in-situ observation of the wear process. Different volume loss rates of the polymer are measured under varying loads and scanning speeds. The tip geometry and contamination are assessed by scanning over a reference sample and by imaging using transmission electron microscopy. The load and tip geometry data are used to determine contact stresses during the test. This talk will discuss the experimental method and results, and the development of models to describe the relationship between wear volume, applied load, and scanning speed.

10:40am **TR-FrM8 Improving Automotive Engine Efficiency through Tribological Testing**, ***Peter Lee***, Southwest Research Institute **INVITED**

Fuel economy is one of the most important issues facing the automotive industry due to rising fuel costs, the need to conserve fossil fuel and government legislation. Although most of the energy losses are controlled through engine design, there is increasing interest in the role of lubricants in improving fuel economy. Crankshaft bearings can account for up to 40% of total engine friction due to the shear losses in the hydrodynamic lubrication regime and it is for this reason that average lubricant viscosities are reducing. However, this reduction in lubricant viscosity increases the frictional losses in boundary contacts in other engine components. In order to reduce this negative impact on fuel economy, engine manufacturers and lubricant and additive suppliers invest heavily in developing novel coatings, base oils and additives to reduce the frictional losses in these contacts.

ASTM have a test method for measuring fuel economy using a 2009 3.6L V6 General Motors gasoline engine. The fired engine test (ASTM D7589) runs for 100 hours using external lubricant heating/cooling systems and a ‘flying flush’ system for changing lubricants without engine shutdown. It compares a baseline lubricant with the test lubricant and measures the fuel economy improvement. However, such engine testing is expensive and hence all companies screen lubricants and coatings prior to running full engine tests.

Lubricants and coatings are screened in commercially available tribometers that are developed to replicate the contact geometries present in the engine. Reciprocating tribometers are used to replicate piston assembly and liner interactions and rotating tribometers are used to replicate camshafts and bearings. Test components may be standard test parts or manufactured from the real engine parts, and lubricant supply may be changed during the tests. In addition to this, engine specific test rigs are often designed and developed. These utilize real engine components operated in the same manner and in the same environment that they experience in the engine without using the full fired engine. Examples of test rigs, test parts and test results showing what can be achieved with these tribometers and test rigs will be presented.

An additional step in tribological testing is the use of single cylinder fired research engines. A specially developed test engine, capable of measuring the friction in the inlet and exhaust overhead valvetrains as well as the piston assembly will be presented along with example data.

11:20am **TR-FrM10 *In Situ* Study of Growth Mechanisms and Kinetics of ZDDP Antiwear Tribofilms in Nanoscale Single-Asperity Contacts**, ***NityaNand Gosvami***, University of Pennsylvania, *J.A. Bares*, BorgWarner Powertrain Technical Center, *F. Mangolini*, University of Pennsylvania, *A.R. Konicek*, *A.M. Schilowitz*, *D.G. Yablon*, ExxonMobil Research and Engineering, *R.W. Carpick*, University of Pennsylvania

Zinc dialkyldithiophosphates (ZDDPs) are lubricant additives used nearly universally in engine oils. Despite the generation of volatile phosphorous- and sulphur-containing compounds in the downstream gases that can reduce the working life of the catalytic converter, the unrivaled wear protection of ZDDPs makes them essential to lubricant performance. ZDDPs work by decomposing under tribological sliding to form nanoscale anti-wear films whose growth mechanisms are still poorly understood due to the complexity of the macroscopic multi-asperity sliding interfaces and the multiple chemical species involved (1). Greater understanding of the formation of these films is essential to enable rational design of more environmentally-friendly and energy-efficient engine oil formulations (2, 3). Here we report the development and application of a novel experimental approach using atomic force microscopy (AFM) for visualizing and quantifying the formation of ZDDP anti-wear films in-situ in a single asperity contact with nanometer-scale spatial resolution. Experiments performed on iron-coated silicon surfaces at 80-140 °C in the presence of ZDDP containing polyalphaolefin oil show that thermal films grow on the substrate in the absence of tribological contact. These films are easily removed by sliding the tip at applied normal forces of only a few nanonewtons (contact pressure < 1.0 GPa). Continued sliding at higher normal loads (contact pressure ~ 2.0 -6.0 GPa) reveals the nucleation and growth of much more robust films with a pad-like lateral structure, similar to the morphology of anti-wear films formed by ZDDP in macroscopic contacts. The growth rate is nonlinear with time, and increases exponentially with temperature and contact pressure, in agreement with reaction rate theory. This is the first direct confirmation of asperity-level formation of such films, and the first quantification of the energetics of the tribofilm growth. Our findings provide new insights into the mechanisms of formation of ZDDP derived anti-wear films, enabling us to directly compare with atomistic predictions of pressure-induced cross-linking of zinc polyphosphates (4) and other possible proposed mechanisms (1).

(1) H. Spikes, Tribology Letters 17 (2004) 469.

(2) H. Spikes, Lubrication Science 20 (2008) 103.

(3) H. A. Spikes, Lubrication Science 20 (2008) 77.

(4) N. J. Mosey, M. H. Muser, and T. K. Woo, Science 307 (2005) 1612.

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