

# Tuesday Morning, October 30, 2012

## Tribology Focus Topic

Room: 19 - Session TR+BI-TuM

### Self Healing Coatings, Bio-Inspired Design, and Frictional Properties of Biological Materials

**Moderator:** D. Irving, North Carolina State University, M.O. Robbins, Johns Hopkins University

8:20am **TR+BI-TuM2 Friction at Hydrogel Contact Lens Surfaces, S.S. Perry, S. Huo, A. Rudy, University of Florida** **INVITED**

The surfaces of six types of silicone hydrogel (SH) contact lenses (PureVision®, O<sub>2</sub> OPTIX®, ACUVUE® Oasys®, ACUVUE® TruEye®, Biofinity®, DAILIES TOTAL1®) and the pHEMA-based ACUVUE® 2 have been analyzed using atomic force microscopy (AFM) in aqueous environment. The elastic modulus, frictional, and adhesive properties of each lens were evaluated using calibrated instrumentations, providing a basis for comparing the distinctive surface properties of these lenses. Cantilevers modified with 5- $\mu$ m (diameter) silica colloidal probes were employed throughout the experiments. Elastic modulus was measured by indenting the probe into the surface of the hydrogel in a controlled manner (i.e. approach speed and maximum applied force), such that the maximum indentation depth was restricted to sub-micron levels. A modulus value was obtained by fitting the characteristic force versus indentation behavior to a mathematical model. The frictional force was measured for the sliding contact of the probe and the surface at the length scale of 500 nm and with applied loads up to 20 nN. The friction coefficient was realized by evaluating the linear dependence of friction force on applied normal load. The lenses examined exhibited an order of magnitude difference—from the softest to the stiffest sample—in modulus value, generally reflective of the distinct surface treatments they received during manufacturing. For example, the pHEMA-based ACUVUE® 2 was shown to have a modulus between 100 and 130 kPa, whereas PureVision®'s was an order of magnitude higher in value. The frictional properties of the lenses followed a similar trend in that the lenses with surface treatment, such as PureVision® and O<sub>2</sub>OPTIX®, generally exhibited coefficients of friction five times greater than that of a non-treated lens such as ACUVUE® OASYS®. The elastic modulus and frictional properties of different lenses evaluated on a nanoscopic level by AFM depict a strong correlation between the surface treatments and the apparent mechanical behaviors of the lenses.

9:00am **TR+BI-TuM4 Linking Cartilage Structure, Lubrication, and Osteoarthritis, D.L. Burris, University of Delaware**

Cartilage is known for exceptionally low friction coefficients during sliding, but its wear resistance is arguably more remarkable. Conventional wisdom suggests that cartilage wears gradually with use and that osteoarthritis is the inevitable consequence. This notion is refuted by the scientific literature. Dissections of mature, healthy, and active joints consistently reveal smooth, glossy, damage-free articulating surfaces that can only occur if tissue recovery matches wear. Cartilage recovery is extremely slow due to a lack of vasculature and numerous lubrication mechanisms have been proposed to explain extremely low in-vivo wear rates. Osteoarthritis (OA) is characterized by progressive wear and caused by a system destabilizing input (e.g. biochemistry, acute injury, altered loading, and joint instability). In certain joint-destabilized animal models, for example, a localized defect (~50  $\mu$ m wide) is visible in as little as a week, and bone-on-bone contact occurs on the order of 6 months. Recent studies suggest that interstitial lubrication, a mechanism that reduces frictional and normal stresses by nearly 100X, is the dominant protective mechanism of cartilage. Localized surface damage can disrupt the very specific structural features responsible for the unique interstitial fluid pressurization mechanism. We hypothesize that localized surface damage can initiate OA-like degradation if it is sufficiently disruptive to the interstitial lubrication mechanism. In this paper, we present friction and wear measurements designed to explore this novel mechanical hypothesis of OA initiation and progression.

9:20am **TR+BI-TuM5 Self Healing Materials: A New Approach to Make Materials Perform More Reliably under Harsh Conditions, S. van der Zwaag, M. Valefi, S. Garcia, M.R. de Rooij, Delft University of Technology and University of Twente, the Netherlands** **INVITED**

Currently all engineering materials are designed on the basis of the 'damage prevention' paradigm i.e. the microstructure is designed such that damage forms as late as possible and grows slowly, but no mechanisms are built in which can reduce damage once formed. Materials in nature on the other hand seem optimised on the basis of 'damage management' paradigm, i.e. the occurrence of damage is taken as unavoidable and the material has the

in-built ability to repair the damage during less demanding stages of the loading cycle. In this presentation we will show various approaches to self healing behaviour in a wide range of material classes and also show how self healing concepts can be used to mitigate tribological damage in both ceramics and polymeric materials. The experimental results are supported by a simple mechanical model.

10:40am **TR+BI-TuM9 Surface Analytical and Tribological Characterization of Diamonlike Boundary Films Extracted from Base Mineral and Synthetic Oils, A. Erdemir, O.L. Eryilmaz, Argonne National Laboratory**

In this study, we explored the possibility of deriving carbon-based boundary films directly from base lubricating oils during tribological tests. For this purpose, we first designed and deposited a series of catalytically active nanocomposite coatings on some steel substrates and by adjusting the ratios of softer phases made out of known catalysts and harder nitride phases (that are also catalytically active), we were able to extract carbon-based boundary films from the base oil molecules and deposit them as protective boundary films on rubbing surfaces. Using UV Raman and variety of other surface and structure analytical techniques, we were able to confirm that these boundary films were indeed similar to those diamonlike carbon films that are typically synthesized using CVD and PVD methods. Some of the main characteristics of resultant DLC boundary films were: very low friction coefficients (less than 0.05) even under extreme sliding conditions and very high resistance to wear and scuffing. In this paper, we will provide insight into the structural and chemical nature of these tribofilms and explain fundamental mechanisms for their impressive tribological properties under severe test conditions.

11:00am **TR+BI-TuM10 Data-driven Model for Estimation of Friction Coefficient via Informatics Methods, E.W. Bucholz, University of Florida, C.S. Kong, Iowa State University, K.R. Marchman, F.-Y. Lin, W.G. Sawyer, S.R. Phillpot, University of Florida, K. Rajan, Iowa State University, S.B. Sinnott, University of Florida**

The rapid development of new mechanical assemblies capable of operating in extreme conditions requires the rapid determination/estimation of friction. Often, during the design phase, materials friction coefficients are unknown. Here, data mining and materials informatics methods are used to generate a predictive model that enables efficient high-throughput screening of ceramic materials, some of which are candidate high-temperature solid-state lubricants. Through the combination of principal component analysis and recursive partitioning using a small dataset comprised of intrinsic material properties, we develop a decision tree based model comprised of if-then rules, which estimates the friction coefficients of a wide range of materials derived from the interrelationships between the intrinsic material properties. This predictive model lays the foundation for new studies in predictive modeling and tailoring materials with specific tribological characteristics. It is applied to predict the tribological performance of a range of different materials.

This work is supported by the Office of Naval Research.

11:20am **TR+BI-TuM11 Structure, Lateral Flow, and Self-Healing of a Bound-and-Mobile Lubricant Film, S.H. Kim, Pennsylvania State University** **INVITED**

There have been a significant amount of efforts to develop boundary lubrication films that have the bound and mobile natures at the same time. As an effort to develop a more efficient boundary film lubrication method, a new bound-and-mobile lubricant molecule was synthesized and its lubrication and self-healing capability was studied. Low-molecular-weight silicone molecules with cationic side groups can form bound-and-mobile boundary lubrication film on silicon oxide surface. Both nano- and macro-scale tribological tests revealed superior lubrication performance of the silicone polymer with cationic side chains (called cationic lubricant polymer, CPL) over the neutral silicone oil. The multilayer CPL films exhibited characteristic topographic features due to ionic interactions within the polymeric film. In the macro-scale, the effects of ionic content and environmental condition on self-healing will be discussed to demonstrate the wear resistance and self-healing capability. In the nanoscale, the results of disjoining pressure and viscosity measurements help understand the lateral spreading of the mobile layer and identify the mobile species. The CPL-coated surfaces are hydrophobic which prevents the detrimental effects of humidity on wear of silicon. In addition, the hygroscopic nature of CPL allows humidity to be absorbed into the film, which enhances the self-healing capabilities. By texturing the silicon surface with nanowells, self-healing can be enhanced when the nanowells are filled with CPL. The nanowells serve as CPL reservoirs that are readily available for self-healing within the wear track for faster cycle intervals. However, the nanowells

deteriorate the self-healing from surrounding the contact region due to the refilling of the empty nanowells.

# Tuesday Afternoon, October 30, 2012

## Tribology Focus Topic

Room: 19 - Session TR-TuA

### Molecular Origins of Friction and Wear

Moderator: S.S. Perry, University of Florida

2:00pm **TR-TuA1 Area, Stiffness, Friction and Adhesion of Contacts Between Rough Surfaces**, *M.O. Robbins, L. Pastewka, T. Sharp*, Johns Hopkins University **INVITED**

Many surfaces have roughness on a wide range of length scales that can be described by self-affine fractal scaling. This roughness has profound effects on contact and friction between experimental surfaces. The talk will present results for the load dependence of contact area, contact stiffness and friction for nonadhesive and adhesive surfaces with a self-affine fractal geometry. Simulations retain atomic structure for a few layers of atoms near the surface and use a Greens function method for an elastic continuum to determine the long-range elastic response. Under a broad range of conditions the area of intimate contact  $A_c$  between nonadhesive surfaces and the normal stiffness  $k_N$  are both proportional to the applied load. These quantities are relatively insensitive to the atomic scale structure of surfaces, and even local plasticity. In contrast, atomic structure changes friction and tangential stiffness by orders of magnitude. For weak adhesion and strong roughness the linear relation between area, stiffness and load is retained, but the ratio of area to load increases. A simple scaling law predicts the change in ratio and why putty or tape sticks to walls but stiffer solids do not.

2:40pm **TR-TuA3 Crystallographic Wear Patterns in Ionic Solids**, *B.A. Krick, K.R. Marchman, S.B. Sinnott, W.G. Sawyer*, University of Florida

Ionic solids have simple and well known crystalline structures while spanning several orders of magnitude in wear rates; this makes them excellent candidates for fundamental studies in wear. Wear experiments on the (001) surface of rock-salts, including NaCl and MgO, revealed that the material wear rates have significant dependency on crystallographic wear direction. The materials experienced maximum wear when sliding in the  $\langle 100 \rangle$  family of directions and minimum wear when sliding in the  $\langle 110 \rangle$ . For MgO the wear rate in the  $\langle 100 \rangle$  direction was approximately three times that in the  $\langle 110 \rangle$  direction. Wear experiments were performed at angles relative to the [100] direction in six degree increments revealing wear as a sinusoidal function of direction with 90 degree periodicity. These results offer a direct link between material structure and the wear properties of a material.

3:00pm **TR-TuA4 Measurements of Off-axis Friction Forces**, *K. Kristiansen, X. Banquy*, University of California, Santa Barbara, *H. Zeng*, University of Alberta, Canada, *E. Charrault, S. Giasson*, Universite de Montreal, Canada, *J.N. Israelachvili*, University of California, Santa Barbara

Current measurements of frictional forces are usually done parallel to the sliding direction. However, when the distances between the moving surfaces and the dimensions of the lubricant approach the nanometer scale, the molecular structure and surface asperities can induce significant frictional forces that are not parallel to the sliding direction. We have developed a new sensor-actuator for the Surface Forces Apparatus which can measure forces and move two surfaces relative to each other in all 3 orthogonal directions with force resolution in the  $\mu\text{N}$  range, and distance control in nm range in the normal direction and  $\mu\text{m}$  range in the plane of the surfaces. I will present how "off-axis" (anisotropic) friction forces behave when shearing two atomically smooth crystalline (lattice) surfaces separated by nanometer thick layers of hexadecane. These anisotropic friction forces can induce complex transient and steady-state motions involving displacements perpendicular to the applied force and non-zero velocity at all stages of back-and-forth sliding.

4:00pm **TR-TuA7 Temperature-dependent Atomic-scale Friction and Wear on NaCl(001)**, *X. Zhao, S.S. Perry*, University of Florida

Atomic-scale friction and wear were investigated by scanning a  $\text{Si}_3\text{N}_4$  tip on NaCl(001) with variable temperature atomic force microscopy. In the absence of wear, an exponential increase in friction with decreasing temperature was observed. Atomic scale wear was detected through the formation of surface pits with a single atomic layer deep. From quantitative measurements of atomic displacement, microscopic wear coefficients were found to agree with known macroscopic wear properties of this ionic material. Both friction and wear exhibit a thermally activated behavior with different activation energies corresponding to the different energy dissipation processes. The thermal activation energy for friction and wear is

$\sim 0.12$  eV and  $0.82$  eV, respectively, with wear obviously requiring more energy than friction.

4:40pm **TR-TuA9 Ultra-Low Wear Nanocomposites: How Low Can We Go?**, *A.A. Pitenis, B.A. Krick, J.J. Ewin, W.G. Sawyer*, University of Florida

Polytetrafluoroethylene (PTFE) is an excellent candidate material for solid lubrication applications due to its low friction coefficient and chemical inertness; however, its use is limited due to its high wear rate. Unfilled PTFE is known to suffer from subsurface crack propagation and subsequent delamination during sliding. To combat this high wear mode, fillers of various sizes have been added to a PTFE matrix to increase the wear resistance by typically one or two orders of magnitude by fracture toughening and load support mechanisms. Nanocomposites are the state of the art in ultra-low wear performance in fluoropolymer systems; polymer blends have been shown to achieve nearly zero wear with wear rates below  $1 \times 10^{-8}$  mm<sup>3</sup>/Nm. These low wear rates are consistently accompanied by visually distinct tribofilms at the interface of the bulk material and counterface. Experiments suggest that a combination of mechanical and tribochemical mechanisms are responsible for the development of these tribofilms and consequent ultra-low wear behavior.

5:00pm **TR-TuA10 Direct Measurement of Friction Forces and Shear Strengths at High-Speed Microscopic Contacts using a Probe and Quartz Resonator**, *B.P. Borovsky*, St. Olaf College

We present a study of the frictional properties of microscopic contacts (radius  $\sim 1 \mu\text{m}$ ) in the high-speed regime ( $> 1$  m/s). Energy dissipation and lateral stiffness of the contact are measured with a transverse-shear quartz resonator in contact with a spherical probe. A transition from partial to full slip is observed at a critical amplitude of motion. Elastic and dissipated forces (identified with static and kinetic friction) are quantified and interpreted without the need for complex calibration procedures or detailed models of the interaction. Kinetic friction is observed to be independent of sliding speed. Measurements of the lateral stiffness at very low oscillation amplitudes allow evaluation of the contact area. For an interface subject to boundary lubrication, we find that friction increases sub-linearly with applied load, in direct proportion to contact area. We determine the corresponding interfacial shear strengths. Results from the technique demonstrated here may find application in contexts where high sliding speeds are routinely accessed, such as microelectromechanical systems (MEMS) and simulations of friction using molecular dynamics.

5:20pm **TR-TuA11 Isolating the Adhesive Component of Micro-Scale Rolling Friction via Vapor-Phase Lubrication**, *S. Misra, B. Hanrahan, R. Ghodssi*, University of Maryland, College Park

Microball bearings have been successfully utilized in several micro-machinery applications, providing low friction, low wear contact, long lifetimes, and device robustness. On all size scales, rolling friction arises from a combination of volumetric mechanical properties, surface chemical properties, and bearing geometries. On the micro-scale, surface effects are enhanced relative to volume, and geometries are dictated by microfabrication techniques. Due to these unique factors, there is not a comprehensive understanding of the fundamental source of rolling friction in microscale systems, but adhesion is theorized to dominate. Vapor-phase lubrication has been implemented to change the chemistry of the surface, specifically addressing the adhesive component of micro-scale rolling friction, leading to reduced friction and enhancing the overall understanding of the system. Future microball bearing supported microsystems will benefit from the work presented here due to a greater knowledge of the influence of adhesion on micro-rolling friction.

A custom silicon micro-turbine supported on ball bearings serves as the platform for the study of rolling friction. 440C stainless steel microballs (285 micrometers diameter) are housed in deep reactive ion-etched silicon raceways. The tribological properties of this device have been the focus of numerous previous studies. The micro-turbine is operated such that normal load and turbine speed can be independently controlled for normal load-resolved spin-down friction testing. The spin-down testing methodology reveals the relationship between friction torque and normal load, which is used to understand the fundamental sources of rolling friction. Vapor saturation techniques have been integrated within the turbine actuation scheme by bubbling nitrogen gas through heated liquid and then using it to actuate and provide normal load for the micro-turbine. A condenser is employed before the output to assure no liquid condenses within the raceway.

A water vapor-lubricated micro-turbine has demonstrated a 43% reduction of friction versus dry nitrogen at a normal load of 50mN in spin-down

testing as well as a 37% increase in overall turbine performance. Additionally, with the introduction of vapor, the relationship between friction torque and normal load was fundamentally changed, revealing the significant influence of adhesion to the system. Vapor lubrication adsorbed on the surface of the ball and raceway lowers their surface energies, reducing the effect of adhesion. These results show the first conclusive demonstration of the adhesive component to micro-scale rolling friction by using vapor phase lubrication.

5:40pm **TR-TuA12 Electronic Friction at the Atomic Scale: Conduction, Electrostatic and Magnetic Effects, J. Krim**, North Carolina State University, *I. Altfeder*, Wright Patterson Air Force Laboratory

We have performed a magnetic probe microscopy study of levitation and atomic-scale friction for Fe on YBCO ( $T_c = 92.5\text{K}$ ) in the temperature range 65 - 293 K, to explore electronic contributions to friction at the atomic scale. The samples were prepared with oxygen-depleted surfaces, with thin semiconducting surface layers present atop the bulk. Below  $T_c$ , the friction coefficient was observed to be constant at 0.19 and exhibited no correlation with the strength of superconducting levitation forces observed below  $T_c$ . The friction coefficient exhibited a change in slope within experimental error of  $T_c$  that increased progressively above  $T_c$  and reached 0.33 by room temperature. The results were analyzed within the context of underlying atomic-scale electronic and phononic mechanisms that give rise to friction, and it is concluded that contact electrification and static electricity play a significant role above  $T_c$ . Quartz crystal microbalance studies of sliding friction studies of molecularly thin films in the presence and absence of magnetic fields, were also performed for both paramagnetic oxygen and diamagnetic nitrogen films on substrates in various magnetic states.

[1] I. Altfeder and J. Krim, *J. Appl. Phys.* (2012), in press

Supported by NSF and AFOSR

# Tuesday Afternoon Poster Sessions

## Tribology Focus Topic

Room: Central Hall - Session TR-TuP

## Tribology Poster Session

**TR-TuP1 Nanomechanical and Nanotribological Responses of Si/SiO<sub>2</sub> Interfaces.** *F.-Y. Lin, X. Sun, D.E. Yilmaz, S.R. Phillpot, S.B. Sinnott*, University of Florida

Nanomechanical and tribological responses of semiconductor/gate oxide interfaces have been demonstrated to significantly affect the performance of devices. Here, we use classical molecular dynamics (MD) simulations to investigate these responses at the atomic scale. The simulations utilize the variable charge, empirical charge optimized many-body (COMB) potential to describe the surface interactions and mechanical responses occurring within differing contacting interfaces. In particular, the mechanical response during nanoindentation and nanoscratching of a Si tip on SiO<sub>2</sub> and HfO<sub>2</sub> thin films is investigated to determine the influence of thin film structure and type on the measured properties as a function of normal load. In addition, the responses of crystalline and amorphous Si/SiO<sub>2</sub> sliding contacts are examined and the impact of operating environment and interfacial charge transfer on the tribological properties is explored.

This work is supported by the Office of Naval Research (N000141010165) and the National Science Foundation (DMR-1005779).

**TR-TuP2 Origin of a Broad Band Emission in Triboluminescence during Friction between Diamond and Quartz in a Gas: Contribution of a Micro-discharge caused by Triboelectricity.** *T. Miura*, National Institute of Occupational Safety and Health, Japan, *E. Imai, I. Arakawa*, Gakushuin University, Japan

The origin of triboluminescence of solid in air has been believed to be essentially photoluminescence excited by ultraviolet light from nitrogen discharge caused by triboelectricity (see Walton's review, *Adv. Phys.* Vol. 26 (1977) p.919.). In this study, we propose that electron-impact is a major and significant origin of the solid luminescence.

The experiment of friction between quartz and diamond was performed in rare gases or nitrogen by a pin-on-disk equipment in a vacuum chamber. A spatial distribution of the triboluminescence was observed by a microscope through the quartz disk and its spectrum was measured by a spectrometer.

Typical discrete lines due to the light emission of the gas discharge and a broad band (wavelengths of 300-600 nm) were observed in the triboluminescence spectrum. The microscopic measurement made it clear that the gas discharge occurred in a gap between quartz and diamond around the contact point and the broad band was emitted at the same place of the gas discharge.

By changing the gas pressure, however, we found that the discharge light almost vanished in the pressure range of 30-100 Pa of nitrogen, while the broad band emission intensely appeared in this range. The broad band intensity became a maximum when a mean free path of electron in plasma was close to the gap distance of the discharge.

It has been known that the quartz was negatively electrified by friction with diamond. We have performed cathode-luminescence experiment for the same diamond sample. A broad band appeared in the spectrum of the cathode-luminescence was identical to the broad band of the triboluminescence.

In conclusion, gas discharge caused by triboelectricity induces cathode-luminescence of the solid. This is the main cause of the broad band in the triboluminescence. Contribution of the ultraviolet light of the nitrogen discharge to the solid luminescence, in contrast, is negligible.

**TR-TuP3 Frictional Study of Carbon Nanotube Arrays Grown on Artificial Hip Joint Metal Surfaces.** *M. Yoshimura, K. Suniya*, Toyota Technological Institute, Japan

At present, a well-designed hip joint has a lifetime of 10-15 years. Since this is rather short compared with an increasing lifetime of human, there is great need to improve the durability and clinical lifetime of artificial joints. Reduction of wear debris through the coating of the material surface is one of methods to improve the durability. Here we grow carbon nanotube (CNT) array and composite film (CNT terminated with graphite layers) on the artificial bone surface (ASTM F75 (Co: 62 wt%, Cr: 30 wt%, Mo: 5 wt %)), and examine the tribological property by scratch measurement.

Alcohol chemical vapor deposition (ACVD) was employed to grow CNT arrays and composite films. Growth temperature, pressure and time were 800 C, 160 torr and 5 min. Ball-on-plate type tribo-test machine

(Tribostation Type 32, Shinto Sci. Co., Ltd.) was employed. Normal loads were set at 50 g or 1 g. According to the recipe [1], CNT arrays standing perpendicular to the substrate and composite films were successfully grown on the ASTM surface. Tribological measurement with 50 g load reveals that both carbon film gives lower friction coefficient than a bare ASTM surface. In addition, CNT arrays showed a smaller friction than the composite films. SEM images of both surfaces after wear experiment under 1 g load show that CNT arrays fall flat to the substrate, and that cracks form in the graphite layers of the composite films. This study demonstrates possible use of CNTs as a solid lubrication for artificial hip joint metal materials.

[1] Y. Matsuoka et al., *J. Vac. Sci. Technol.* B29, 061801 (2011).

**TR-TuP6 Comparative Study of Tribocorrosion Behavior of Biomedical Alloys Coated with Metal-Ceramic Multilayers.** *M. Flores, O. Jimenez, E. Rodriguez*, Universidad de Guadalajara, Mexico, *L. Huerta*, Universidad Nacional Autonoma de Mexico

The tribocorrosion behavior of Ti6Al4V and CoCrMo alloys alone and coated with TiAlN/TiAl multilayers was investigated. The multilayers were deposited onto the alloys by magnetron sputtering. The structure and composition of multilayers were studied by means of XRD and RBS techniques respectively. The tribocorrosion was performed using a ball-on-flat reciprocating tribometer, the tests were conducted in a simulated body fluid at  $36.5 \pm 1$  °C of temperature and 7.4 Ph. The loads used were between 1N and 5N, the oscillating frequency was 1Hz. The counterparts were Al<sub>2</sub>O<sub>3</sub> balls 10 mm in diameter. The tribocorrosion and corrosion were studied using electrochemical techniques such as open circuit potential (OCP), electrochemical noise, potentiodynamic and potentiostatic polarizations in a simulated body fluid. The individual and synergistic effects of wear and corrosion on total wear loss were estimated. The worn surface was studied by means of profilometry. For the used conditions the CoCrMo alloys shows a high tribocorrosion resistance respect to the Ti6Al4V. The results indicate that multilayers improve the tribocorrosion resistance of both alloys.

# Wednesday Morning, October 31, 2012

## Tribology Focus Topic

Room: 19 - Session TR+SE-WeM

## Tribology and Wear of Low-Friction Coatings and Materials

Moderator: D.L. Burris, University of Delaware

8:00am **TR+SE-WeM1 Seeing Things as They Really are: *In Situ* Studies of Materials in Application Environments and the Development of Temperature-Adaptive Nanocomposites**, C. Muratore, Air Force Research Laboratory, J.J. Hu, J.E. Bultman, UDRI/Air Force Research Laboratory, A.A. Voevodin, Air Force Research Laboratory **INVITED**

In the early 1940s, military pilots and those who serviced their planes were surprised by serious problems with ignition systems and diverse electrical troubles in their state of the art aircraft. Further study revealed that the graphite commutator brushes used in the electrical generator on the airplane (similar to the alternator in our automobiles) were the source of these technical difficulties, because they wore out 100 to 1000 times faster than expected. Over 70 years later, sensitivity of materials at contact interfaces to the extreme ambient environments aircraft are subjected to is still limiting aerospace capability. One of the reasons materials scientists haven't overcome these problems sooner is because it is difficult to do materials science, at least the part where you correlate performance to structure and composition, when there is such a big difference between the operating environment and the environment in which analysis is conducted. All the materials tribologist can really do is *post mortem* forensics work on materials designed to get hot after they have cooled down to a convenient handling temperature. During that cooling down time, phase changes and grain growth occur, perhaps misleading the researcher on the compounds or phases yielding high or low friction at interfaces in relative motion. In this talk we will review innovative characterization techniques designed to provide the insight necessary to produce environmentally adaptive tribological coatings, especially materials designed to operate over broad ranges of humidity (i.e., earth to space) and temperature (i.e., ignition to supersonic flight). Characterization of temperature adaptive nanocomposite lubricant materials, such as MoN/Ag and VN/Ag via Raman spectroscopy will be reviewed in depth.

8:40am **TR+SE-WeM3 Tribological Surface Chemistry of Model Lubricant Additives Measured in Ultrahigh Vacuum**, W.T. Tsao, University of Wisconsin Milwaukee

Additives are generally added to lubricants, which react with the surfaces to form a boundary lubricating film that can lower friction and/or prevent wear. At the high interfacial temperatures that occur under so-called extreme-pressure conditions, the surface reaction and film growth kinetics are dominated by thermal processes. In contrast, it is postulated that, under mild conditions, where the surface temperature rise is low, a surface film can be formed by a shear-induced, surface-to-bulk transport mechanism. This effect is investigated by studying the tribologically induced surface reactions of model sulfur- and boron-containing additives on copper surfaces in ultrahigh vacuum (UHV) where the background pressure is  $\sim 1 \times 10^{-10}$  Torr. The nature of the initial surface species that are formed by exposure of the copper surface to the model lubricant additive is investigated using a range of surface analytical techniques such as temperature-programmed desorption (TPD), reflection absorption infrared spectroscopy (RAIRS) and X-ray photoelectron spectroscopy (XPS). This enables the nature of the initial surface species to be identified, and their thermal stability to be measured in some detail. The effect of rubbing these adsorbate-covered surfaces is investigated, also in UHV, by measuring the friction coefficient and contact resistance during rubbing. The chemical composition of the wear track is followed using high-spatial-resolution Auger spectroscopy to follow the fate of the surface species caused by rubbing and to test the above postulate.

In addition, the effect of low-coordination sites formed on the surface by rubbing on the reactivity of gas phase lubricants is explored and finally, this strategy is used to understand the tribochemistry of borate esters on copper under mild rubbing conditions.

9:00am **TR+SE-WeM4 Nanomechanical and Nanotribological Properties of ZnO Thin Films**, E. Broitman, L. Martínez de Olcoz Sainz, Linköping University, Sweden, C. Bojorge, Cinso, Citedef-Conicet, Argentina, J.B. Miller, Carnegie Mellon University, H. Canepa, Cinso, Citedef-Conicet, Argentina, L. Hultman, Linköping University, Sweden

During the last years, with the advances in nanotechnology, zinc oxide (ZnO) thin films have attracted an increased attention for applications as

sensor devices in microelectromechanical systems. In these applications, where high mechanical stress could be imparted on the film in contact situations, the knowledge of the coating nanomechanical and nanotribological properties is critical since they will affect the functions and durability of the films. Sol-gel method is a simple and low cost process for the fabrication of ZnO thin films; interestingly, there are only two publications partially dealing with their mechanical and tribological properties.

In this work, we studied ZnO thin films grown on glass substrates by sol-gel process. Single and multilayered films were deposited by spin-coating technique onto glass substrates, and subsequently transformed into nanocrystalline films using different thermal treatments  $T_t$ .

The microstructural properties and morphology of the films have been studied by X-ray diffraction (XRD), scanning electron microscopy, and surface probe microscopy. XRD patterns of films dried at room temperature show features characteristic of layered basic zinc acetate, a lamellar ZnO precursor, consisting of zinc hydroxide hydrate sheets separated by intercalated acetate groups. At higher  $T_t$ , ZnO diffraction patterns are dominated by features corresponding to the (100), (002) and (101) reflections of the crystalline zinc oxide "wurtzite" structure. The higher relative (002) intensity in some films is evidence of preferential growth of the structure along the c-axis, the axis of symmetry in the wurtzite structure.

The nanomechanical and nanotribological properties were measured by a Triboindenter TI-950 from Hysitron. The hardness  $H$  and reduced Young's modulus  $E_r$  of the ZnO thin films were investigated by nanoindentation measurements with a Berkovich indenter at peak loads of 150  $\mu\text{N}$ . The films with the lower  $T_t$  exhibit a wide dispersion in the values due to the inhomogeneities on the degree of coating crystallinity. At the higher temperatures, the dispersion vanishes and we obtained  $H = 5.6$  GPa and  $E_r = 99$  GPa. We also observed at low temperatures the presence of pop-in events that can be associated to the presence of the multilayers. The friction coefficient was measured at ambient conditions using a conical diamond tip in a reciprocal test, applying a normal force of 10  $\mu\text{N}$  and a stroke distance of 10  $\mu\text{m}$ . The friction coefficient decreases from 0.37 to 0.30 when  $T_t$  is increased. The different mechanical and tribological properties can be correlated to the changes in the microstructure upon different heat treatments.

9:20am **TR+SE-WeM5 Tribological and Compositional Properties of Electroless Nickel-Boron Coatings Annealed at Various Temperatures**, K. Gilley, University of Florida, Y. Riddle, UCT Coatings Inc., S.S. Perry, University of Florida

In this study, the tribological and compositional properties of annealing temperatures on electrolessly deposited nickel boride coatings were investigated. All samples were coated in the same bath and had approximately the same starting composition: 31 atomic % Ni, 19 atomic % B, 42 atomic % O, and 8 atomic % C. Samples were annealed at temperatures of 250°C, 400°C, 550°C, and 700°C under a constant flow of oxygen. The tribological properties of the samples were tested using a novel pin-on-disc tribometer. The pin-on-disc tribometry was performed in air under ambient RH conditions, keeping conditions the same throughout all tests that were performed. The influence of the annealing temperature on surface composition was studied by X-ray photoelectron spectroscopy (XPS), used to identify and relatively quantify the elements present. Raman spectroscopy was used to differentiate between chemical species that were indistinguishable in XPS. Increasing annealing temperatures were seen to influence the tribological properties of the coatings to a large degree; with the samples with higher annealing temperatures having a significantly lower coefficient of friction,  $\mu \approx 0.16$  for the sample annealed at 550°C and  $\mu \approx 0.06$  for the sample annealed at 700°C, than the lower temperature annealed samples,  $\mu \approx 0.5$  for samples annealed at 250°C and 400°C. Similarly, the chemical nature of the coatings were strongly affected by the differing annealing temperatures; with the higher annealing temperature samples showing heavy oxidation and migration of boron to the surface, while the lower annealed samples remained largely unchanged. The lowering of the friction coefficient in the samples annealed at 550°C and 700°C was attributed to the migration and subsequent oxidation of boron forming low friction  $\text{B}_2\text{O}_3$  at the surface.

10:40am **TR+SE-WeM9 First Contact: SPR and SERS Studies of the Initial Transfer Behavior of PTFE**, K.L. Harris, B.A. Krick, D.W. Hahn, W.G. Sawyer, University of Florida

Traditionally the tribological behavior of PTFE (polytetrafluoroethylene) has been studied in the steady state after many sliding cycles. Steady state

studies neglect events that occur during the first contact and sliding cycles, as well as the early transient behavior of PTFE. In-situ surface plasmon resonance (SPR) tribology experiments allow for the observation of initial transfer after the first contact and first sliding cycle of PTFE. SPR showed transfer of PTFE after the first cycle of sliding, contrary to previous models of films formed by delamination wear debris. Surface enhanced raman spectroscopy (SERS) verified the chemical identity of the transfer film. Friction behavior of PTFE was shown to differ in the first cycle from the behavior seen after a transfer film was created and to depend on contact pressure and sliding speed.

11:00am **TR+SE-WeM10 Tribological Investigations of Octadecylphosphonic Acid (ODP) and Octadecyltrichlorosilane (OTS) Self-Assembled Monolayers: A Comparative Study of MEMS-type Interfaces**, *N. Ansari*, Auburn University, *S. Barkley*, *C. Bouxsein*, *M. Deram*, *N. Eigenfeld*, St. Olaf College, *O. Matthews*, Luther College, *A. Poda*, *W.R. Ashurst*, Auburn University, *B.P. Borovsky*, St. Olaf College, *E. Linn-Molin*, *E.E. Flater*, Luther College

Since microelectromechanical systems (MEMS) are critically-limited by interfacial phenomena such as friction and adhesion, strategies have been developed to reduce friction in these systems. One common strategy is to coat MEMS surfaces with molecularly-thin self-assembled monolayer (SAM) coatings. Silicon MEMS are most commonly coated with silane-based SAMs, such as octadecyltrichlorosilane (OTS). Continued development of MEMS technology may require new material systems to be employed. Therefore, in this study, we investigate the frictional properties of octadecylphosphonic acid (ODP) monolayers deposited on aluminum oxide surfaces. Measurements using an atomic force microscope (AFM) and separately using a nanoindenter-quartz crystal microbalance system were performed each with a microsphere-terminated probe, allowing for a comparative study between different velocity regimes using contacts with similar sizes, surface roughnesses, and interfacial chemistries. AFM colloidal probe friction measurements indicate that while the frictional properties of aluminum oxide can be reduced with the use of an ODP monolayer, a more dramatic rubbing-induced modification is clearly evident for both bare and SAM-coated aluminum oxide substrates. These modification effects depend on scanning duration and environmental conditions such as humidity. We hypothesize that a tribochemical reaction occurs between aluminum oxide and ambient water, which has also been observed in macroscopic tribological studies of aluminum oxide published in the literature.

11:20am **TR+SE-WeM11 Diffusion of Gold Islands on Graphene**, *B. Dawson*, *M. Lodge*, *M. Ishigami*, University of Central Florida

Recent theoretical work has suggested that gold nanoclusters on graphite can exhibit both diffusional friction and a novel ballistic friction behavior [1]. This ability to tune friction at nanoscale interfaces can be useful for developing nanoscale motors and machines in general. Furthermore, understanding this nanotribological behavior can be utilized for various nanomechanical devices fabricated from graphene, which is chemically identical to graphite.

We have measured the frictional energy dissipation of gold nanoclusters on graphene as a function of temperature and cluster size using the quartz crystal microbalance (QCM) ring-down technique. By measuring this dissipation, it is possible to quantitatively measure the island diffusion coefficient and precisely monitor how the diffusion and slip time change with temperature, and directly compare these results with the recent theoretical studies. In addition, our measurements give insight into the nanotribological properties of a two dimensional material studied at higher sliding speeds than typically accessible using atomic force microscopy.

[1] R. Guerra *et al.* Nature Materials **9**, 634 (2010).

11:40am **TR+SE-WeM12 Synthesis and Tribology of MoS<sub>3</sub> Nanoparticles**, *J.R. Lince*, The Aerospace Corporation, *A.M. Pluntze*, Colorado State University, *S.A. Jackson*, The Aerospace Corporation

There has been recent interest in the use of solid lubricant nanoparticles in coatings and as boundary additives in liquid lubricants. Examples include nanoparticles of MoS<sub>2</sub> and WS<sub>2</sub>. The formation of these nanoparticles is nontrivial, requiring techniques such as gas phase syntheses and electric discharges. We are exploring simpler syntheses using wet chemical techniques. In particular, the synthesis of MoS<sub>3</sub> nanoparticles involves hydrothermal reaction between molybdate salts and sodium sulfide under controlled pH conditions.<sup>1</sup>

The use of MoS<sub>3</sub> as a tribological material has not been explored beyond its use as an oil additive.<sup>2</sup> We are investigating its potential for use in solid lubricant coatings. Bonded MoS<sub>2</sub> coatings experience widespread usage for

lubricating mechanisms on virtually every spacecraft (i.e., using micron-sized MoS<sub>2</sub> particles). We formulated resin-bonded coatings using MoS<sub>3</sub> nanoparticles as the lubricating pigment, and compared their tribological performance to commercial bonded MoS<sub>2</sub> coatings. Surprisingly, the MoS<sub>3</sub>-formulated coatings performed similarly to the MoS<sub>2</sub>-based coatings. Specifically, they showed similar coefficients of friction (i.e., 0.04 to 0.06) and endurance in dry nitrogen (<0.1% RH). We will present results of surface analyses on worn coatings to reveal changes in composition and chemical state of the MoS<sub>3</sub> that might explain the measured low friction. In addition, results of tribological performance in humid air atmospheres will be presented.

We have also explored syntheses of MoS<sub>2</sub> nanoparticles using nanosize MoS<sub>3</sub> as a starting material. A recent study purported to create MoS<sub>2</sub> nanoparticles with the addition of an aqueous reducing agent during hydrothermal synthesis of MoS<sub>3</sub>.<sup>3</sup> However, X-ray fluorescence analysis of the product of our synthesis showed that the S:Mo remained at 3.0 after using the reducing agent. Other conversion methods including vacuum reduction of the MoS<sub>3</sub> nanoparticles will be discussed.

References:

1. P. Afanasiev, "Synthetic approaches to the molybdenum sulfide materials," *Comptes Rendus Chimie*, 11(1-2) (2008) 159-182.
2. O.P. Parenago, V.N. Bakunin, G.N. Kuz'mina, A.Yu. Suslov, and L.M. Vedeneva, "Molybdenum Sulfide Nanoparticles as New-Type Additives to Hydrocarbon Lubricants," *Doklady Chemistry*, 383(1-3) (2002) 86-88.
3. Y. Tian, X. Zhao, L. Shen, F. Meng, L. Tang, Y. Deng, Synthesis of amorphous MoS<sub>2</sub> nanospheres by hydrothermal reaction," *Materials Letters* 60 (2006) 527-529.

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# Wednesday Afternoon, October 31, 2012

## Late Breaking Session

Room: 14 - Session LB+EM+GR+MN+TR-WeA

## Select Topics in Surface and Interface Science

Moderator: C.R. Eddy, Jr., U.S. Naval Research Laboratory, J.M. Fitz-Gerald, University of Virginia

2:00pm **LB+EM+GR+MN+TR-WeA1 Degradation Kinetics of Hard Gold Tribofilms**, N. Argibay, M.T. Dugger, M.T. Brumbach, S.V. Prasad, Sandia National Laboratories

Hard gold coatings are low alloy (> 98% Au) films exhibiting relatively low friction, electrical contact resistance (ECR) and chemical reactivity, making them uniquely suited for use in dynamic electrical connections. Hardness is primarily a result of grain refinement achieved through alloying. At relatively low temperature (approx < 0.5T<sub>m</sub>) the diffusion of codeposited and underlayer species toward the free surface, dominated by grain boundary and pipe diffusion, has been identified as a principal degradation pathway. The consequent formation of metal oxides deteriorates ECR and often contributes to increased wear and friction. A clear antagonistic relationship exists between the hardening mechanism that improves tribological performance and the diffusion phenomena that reduce useful lifespan. This talk focuses on the role of diffusion and film morphology on the aging and degradation of the tribological and electrical characteristics of hard gold films.

2:20pm **LB+EM+GR+MN+TR-WeA2 Effect of Nitrogen Concentration on the Surface Properties of Plasma Nitrided Tool Steels**, P. Abraha, J. Miyamoto, Meijo University, Japan

The nitriding of tool steel was performed in electron beam excited plasma using neutral nitrogen species and nitrogen ions. The plasma apparatus is composed of three regions: the discharge region, the acceleration region and the processing region. This set up has the advantage of controlling the energy and number of electrons involved in producing the plasma independently.

In this study, the control of the nitrogen concentration on the formation of the hard but brittle compound layer and the effect on the tribology of the tool steel surface were investigated. Electron probe micro-analyzer (EPMA) results revealed that nitrogen concentration of samples nitrided by neutral nitrogen species had deep diffusion layer before reaching the threshold value of 6% nitrogen concentration that is necessary for the formation of the compound layer. Whereas in the samples nitrided by nitrogen ions, compound layer was confirmed right from the onset of the nitriding process.

The results of our experiments show that in nitriding the tool steel for 6h, below the threshold value, a mirror finish surface (Ra=14nm) with a deep diffusion layer of (up to 80 micrometers) and a surface hardness of more than two times (1300 Hv) that of the untreated sample (600 Hv) were produced. Our results demonstrate that neutral species based nitriding is effective for high performance and high precision mechanical components that require high hardness and wear resistance without altering the as finished dimensional accuracy, surface roughness and appearance.

2:40pm **LB+EM+GR+MN+TR-WeA3 High Strength Carbon Fiber Composite Wafers for Microfabrication**, L. Pei, K. Zufelt, R. VanFleet, R.C. Davis, J. Lund, K. Jones, B.D. Jensen, Brigham Young University, J. Abbott, M. Harker, M. Zappe, S. Liddiard, Moxtek

Carbon fiber composites are very high strength materials that could be enabling materials for micro and mesoscale applications. These materials have comparable strength to silicon but are much less brittle and can achieve four times higher strain. Several challenges must be overcome before carbon fiber composite devices can be fabricated on this scale. One challenge is the fabrication of ultra-thin wafers with low void density and low surface roughness. Another challenge is the ability to reliably machine the material into desired patterns. Here we present a method for curing carbon fiber wafers (~100 μm thick) with low surface roughness, low void density, a modulus of 50 GPa, and a yield strength of ~3.6 GPa. These wafers are suitable for laser machining into high fidelity micro and mesoscale structures. We will present laser micromachined devices made from these wafers including a series of high strength support structures for ultrathin membranes and a high-dynamic-range accelerometer.

4:00pm **LB+EM+GR+MN+TR-WeA7 Selective Graphitization using Multi-Ion Beam Lithography**, J. Fridmann, Raith USA Inc., S. Tongay, University of California, Berkeley, M. Lemaitre, A.F. Hebard, B. Gila, University of Florida, A. Nadzeyka, Raith GmbH, Germany, F. Ren, X. Wang, University of Florida, D.K. Venkatachalam, R.G. Elliman, Australian National University, Australia, B.R. Appleton, University of Florida

Promising techniques for growing graphene on SiC single crystals for electronic device fabrication include heating in UHV above the graphitization temperature (T<sub>G</sub>)<sup>1</sup>; or processing them in vacuum using pulsed excimer laser<sup>2</sup>.

We report recent findings on the graphitization of SiC using a patterned Ga implantation, in which the implanted regions exhibit reduced T<sub>G</sub> and enhanced graphitization above T<sub>G</sub>. Here we report an approach that combines ion implantation, thermal or pulsed laser annealing (PLA), and multi-ion beam lithography (MIBL) to both pattern and synthesize graphene nanostructures on SiC single crystals at low temperatures. This approach utilizes a MIBL system developed at the University of Florida in collaboration with Raith for implantation/nanofabrication, in combination with thermal annealing in vacuum or PLA with a 25 ns pulsed ArF laser in air. To investigate the mechanisms and the effects of the implanted species, ion damage, and annealing, samples were also subjected to broad-area ion-implantations using facilities at the Australian National University.

It has recently been shown that implantation of Si, Ge, Au, or Cu followed by thermal annealing in vacuum below the T<sub>G</sub> of SiC can selectively grow graphene *only* where the ions are implanted, and that graphene nanoribbons a few nanometers to microns wide can be formed using MIBL<sup>3</sup>. Additionally, we will show that graphene can be formed on implanted and/or unimplanted SiC by ArF PLA in air, at fluences from 0.4-1.2 J/cm<sup>2</sup>. AES, SEM, X-sectional TEM, micro-Raman analyses and heat flow simulations are presented to verify graphene growth and explain the effects and mechanisms involved.

1. C. Berger, Z. Song, T. Li, X. Li, A. Y. Ogbazghi, R. Feng, Z. Dai, A. N. Marchenkov, E. H. Conrad, P. N. First, and W. A. de Heer, J. Phys. Chem. 108, 19912 (2004)

2. Sangwon Lee, Michael F. Toney, Wonhee Ko, Jason C. Randel, Hee Joon Jung, Ko Munakata, Jesse Lu, Theodore H. Geballe, Malcolm R. Beasley, Robert Sinclair, Hari C. Manoharan, and Alberto Salleo; ACS Nano Vol.4, No. 12, 7524-7530 (2010).

3. S. Tongay, M. Lemaitre, J. Fridmann, A. F. Hebard, B. P. Gila, and B. R. Appleton, Appl. Phys. Lett. 100, 073501 (2012).

4:20pm **LB+EM+GR+MN+TR-WeA8 Unripppling and Imaging of Extra-Large Free-Standing Graphene with Atomic Precision**, W.W. Pai, R. Breitweiser, Y.C. Hu, Y.C. Chao, National Taiwan University, Taiwan, Republic of China, Y.R. Tzeng, Institute of Nuclear Energy Research of Taiwan, Republic of China, L.J. Li, Academia Sinica, Taiwan, Republic of China, K.C. Lin, Catholic Fu Jen University, Taiwan, Republic of China

Nanoscale ripple is believed to be a common feature most manifested in free-standing graphene and is expected to play an important role in altering the coupling of graphene's electronic and geometric structures. Direct characterization of free-standing graphene ripple is challenging from atom-resolved transmission electron microscopy (TEM) due to its limited depth resolution. Recent scanning tunneling microscopy (STM) of free-standing graphene uses small suspended area (1 or 5 microns) samples and can introduce uncontrolled tension that alters the intrinsic graphene structure. Here we report an STM study of suspended extra-large (~4000 micron<sup>2</sup>) Cu CVD graphene that was prepared with a resist-free transfer and characterize its electromechanical response in details. In our study, a series of controlled "Z-V" spectroscopy were carefully conducted. In Z-V spectroscopy, the tip displacement vs. sample bias in close-loop condition is recorded. This gives hints on the nature of interaction forces and the mechanical response of graphene. In contrast to a solid surface, the graphene membrane is very compliant and Z-V curves are characterized by a fast-rise regime and a plateau regime that follows. Graphene deformation up to 100 nm with simply a small ~1 V bias ramp was observed. We discovered that our graphene is in best analogy with a curved rubber band that maintains quasi-static in shape until it is either pulled or pushed to tensile stress regimes. The graphene can be manipulated by the STM tip through electrostatic and van der Waals forces, with the latter being significant when it is repulsive. In its transit to tensile-stressed state, the graphene exhibits a series of sudden speed jump; we interpret these events as unrippling of graphene ripples and render support with molecular dynamics (MD) simulation. Atom-resolved graphene images provide direct evidence of nanoscale structure ripples in its intrinsic state and the smoothing out of such ripples in the tensile regimes. Surprisingly, on rippled monolayer graphene,



coexistence of triangular and hexagonal graphene lattices without tip condition change were observed. Our study provides a foundation to understand and control the electromechanical response of graphene (or other flexural atomic crystals) in its pristine two-dimensional form when subjected to a local proximal probe, therefore paves way to further investigate its structure-property correlation with atomic precision.

4:40pm **LB+EM+GR+MN+TR-WeA9 Ultrafast Charge Transfer at Monolayer Graphene Surfaces with Varied Substrate Coupling.** S. Lizzit, ELETTRA Sincrotrone Trieste, Italy, R. Larciprete, CNR, Institute of Complex Systems, Italy, P. Lacovig, ELETTRA Sincrotrone Trieste, Italy, K. Kostov, Bulgarian Academy of Sciences, Bulgaria, D. Menzel, Technische Universität München and Fritz Haber Institute, Germany

The importance and scientific appeal of graphene monolayers (Gr) are out of question, and investigations of its electronic properties abound. Most of these center on the most spectacular region, that around the Dirac cone, which is also the most relevant region for possible devices. But regions outside of this region are also important, since their correct representation requires basic understanding, and since they may relate to applications in photonics, photochemistry, and contact formation. Also, static investigations are more frequent than those of dynamics.

We present here the first investigation of electron dynamics at energies above the Fermi (and Dirac) energy but below the vacuum level [1]. To this purpose we used the core hole clock (CHC) method with adsorbed argon and measured the transfer rate of a localized electron (the 4s electron on core-excited Ar) to the surface of Gr monolayers with variable substrate coupling: strong but graded coupling for Gr on Ru(0001) ("valleys" and "hills"), and decoupled Gr ML on SiO<sub>2</sub>. We obtained the latter system by using the recently developed transfer-free approach [2] based on the synthesis of SiO<sub>2</sub> layers directly below Gr epitaxially grown on Ru(0001), through a stepwise reaction between intercalated silicon and oxygen. This method provides the optimal system to study the electronic properties of Gr using spectroscopic approaches, such as the CHC method.

We find strong variations of CT time between ~3 fs (Gr ML strongly coupled to substrate on Ru(0001) "valleys") and ~16 fs (decoupled Gr on SiO<sub>2</sub>). A ratio of 1.7 is found between the "hills" and "valleys" of the corrugated Gr/Ru. The very fast CT on Gr/Ru valleys is interpreted as due to hybridized Ru orbitals "reaching through" the Gr layer which change with the relative Gr/Ru alignment and distance. On the decoupled Gr layers the intrinsic coupling to the Gr empty  $\pi^*$  states determines the CT time. The intermediate CT time for the Gr hills on Ru shows that these regions are far from the "decoupled" condition. The results contribute new information on the still controversial states of Gr/Ru, and shed light on the empty density of states above Gr surfaces and the coupling to them in an energy range possibly important for photonic applications of Gr, such as solar energy conversion.

[1] S. Lizzit, R. Larciprete, P. Lacovig, K.L.Kostov, D. Menzel, *in preparation*

[2] S. Lizzit *et al.* Nanoletters (2012) DOI: 10.1021/nl301614j

5:00pm **LB+EM+GR+MN+TR-WeA10 Fano Interference Effects in Hydrogen Intercalated Graphene.** A. Boosalis, T. Hofmann, University of Nebraska-Lincoln, R. Elmquist, M. Real, National Institute of Standards and Technology (NIST), M. Schubert, University of Nebraska-Lincoln

Graphene has been the focus of much recent research due to its unique electronic and optical properties, with potential for high performance electronics, tunable ultra-fast lasers, and transparent electrodes. Further development of graphene for commercial use requires effective large-area epitaxial production that maintains the desirable properties of exfoliated graphene. One such method of epitaxial graphene growth is thermal sublimation of Si from SiC. Sublimation of Si from the Si-face (0001) is the most controllable but produces a  $(6\sqrt{3} \times 6\sqrt{3})R30^\circ$  surface reconstructed layer prior to graphene formation. This layer can be altered by subsequent hydrogen intercalation, resulting in quasi-free-standing (QFS) epitaxial graphene.

In order to determine the effect of hydrogen intercalation on the optical properties of graphene we performed spectroscopic ellipsometry experiments in a spectral range of 3 to 9 eV before and after hydrogen intercalation of buffer layer only carbon growth on 6H SiC (0001). Spectroscopic ellipsometry is a widely used technique for determining the optical properties of thin films, and can provide sensitivity to film quality, morphology, and strain. In the case of graphene sensitivity is obtained through the critical-point (CP) located at 5.1 eV and modified by a Fano interference. Analysis of absorption near the CP is achieved through a parameterized model dielectric function (MDF) which is varied until a best-match between model and experimental data is obtained.

Best-match model results show drastic changes in the imaginary part of the MDF between previous measurements of buffer layer only growth on SiC,

and buffer layer growth after hydrogen intercalation. Buffer layer only growth exhibits a far greater absorption throughout the spectrum, with an exciton produced maximum energy point that is shifted toward the infrared from the CP energy. After hydrogen intercalation, the QFS graphene layer exhibits a lowered absorption with a maximum closer to that of the CP energy; displaying an MDF closer to that of theoretical predictions for graphene.

In conclusion, hydrogen intercalation of buffer layer carbon growth on SiC (0001) has been shown to produce QFS graphene with optical properties closest to that of theoretical predictions for graphene, further proving its effectiveness as a tool for large-area epitaxial graphene production. In addition, buffer layer carbon growth shows optical properties sufficiently different from that of graphene to allow spectroscopic ellipsometry to become a viable in-situ monitor for commercial production of hydrogen intercalated graphene on SiC.

5:20pm **LB+EM+GR+MN+TR-WeA11 In Situ Dry-Cleaning of Ge(100) Surface using H<sub>2</sub>O<sub>2</sub>.** K. Kiantaj, T. Kaufman Osborn, T.J. Kent, A.C. Kummel, University of California San Diego

Since Ge has higher hole and electron mobility compared to silicon, it is a good candidate for development of a new channel material in CMOS semiconductor devices. One of the obstacles in using Ge as a channel material is the high interface trap density between Ge and Ge native oxide. Air exposed Ge surfaces have a high density of defects and contaminants, but, in order to make optimal semiconductor devices, nearly perfect bonding between each unit cell and the gate oxide layer is required. Although there are many methods available for cleaning the Ge surface, the effectiveness of each of these methods highly depends on the cleanliness of the processing chambers. After cleaning, the Ge surface is typically functionalized with OH groups via water (H<sub>2</sub>O) or hydrogen peroxide (HOOH) during atomic layer deposition of the gate oxide. This OH functionalized surface ideally provides a high density of reactive sites for precursor nucleation. We have studied the effect of a very small amount of hydrocarbon in the processing chambers, and its effect on both the clean Ge surface and the OH functionalized surface since this may increase the density of interface traps and limit Equivalent Oxide Thickness (EOT) scaling. In-situ cleaned Ge surfaces as well as HOOH dosed surfaces have been studied after exposure to hydrocarbon contaminants with x-ray electron spectroscopy (XPS) and scanning tunneling microscopy (STM). An Argon ion source sputtering system was employed for in-situ cleaning of the Ge surface. After exposure to trace hydrocarbon contaminants, two different nanoscale features were observed by STM on the Ge and HOOH/Ge surfaces. One type of contamination denoted as carbon "nanoclusters" which are typically 0.3-0.5nm in height and 2-4nm in diameter. A distinctly different feature is observed on the Ge-OH terminated surface denoted as carbon "nanoflakes". In contrast to nanoclusters, nanoflakes were only observed on the Ge surfaces dosed with low concentration hydrogen peroxide. In the next step, a high concentration hydrogen peroxide source in combination with an ozone source was employed to study the removal of the contaminants from the Ge surface. Several dosing conditions and sample temperatures were studied and optimized. As the result, an atomically clean Ge surface were achieved by employing an all-dry in-situ process. The all-dry cleaning procedure does not involve any ion-milling or wet-cleaning procedures as both of these methods involve surface etching and result in surface roughness which is not desirable for semiconductor devices.

5:40pm **LB+EM+GR+MN+TR-WeA12 Hf-based High-k Dielectrics for Ge MOS Stacks.** S. Fadida, M. Eizenberg, Technion Israel Institute of Technology, Israel, L. Nyns, D. Lin, S. Van Elshocht, M. Caymax, IMEC, Belgium

Ge has drawn much attention recently, being a leading candidate to serve as the channel material of future metal oxide field effect transistors (MOSFETs) due to its high carrier mobility with respect to Si. The interest in Ge is mostly because of its high hole mobility. Most of Ge related researches were focused so far on the challenge of Ge surface passivation. In this research we have moved on to the next challenge - finding a suitable high-k dielectric for a Ge-MOS stack. The high-k dielectric has to be chemically and thermally stable on top of the chosen passivation layer, have sufficiently high energy barriers with respect to Ge energy band edges, and have a large dielectric constant in order to obtain the required low effective oxide thickness (EOT). We have studied the chemical, structural and electrical properties of various Hf-based high-k dielectrics: HfO<sub>2</sub>, Hf<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub>, Hf<sub>x</sub>Al<sub>1-x</sub>O<sub>2</sub> and Hf<sub>x</sub>Gd<sub>1-x</sub>O<sub>2</sub>. All high-k dielectrics (4 nm thick) were deposited by atomic layer deposition (ALD) on top of a constant passivation stack composed of a thin GeO<sub>2</sub> layer (0.7 nm thick) followed by a thin (2 nm) ALD Al<sub>2</sub>O<sub>3</sub> layer. The Al<sub>2</sub>O<sub>3</sub> layer, which has high band offsets to Ge and GeO<sub>2</sub>, was added since HfO<sub>2</sub>, as many of the leading candidates for high-k dielectrics, are unstable on top of Ge or GeO<sub>2</sub>. A thorough and systematic electrical and chemical characterization of this complex gate

stack was carried out. The interesting results show that this challenge of seeking for a superior high-k is not detached from the passivation challenge. Surprisingly, we have found that although the passivation stack was kept constant for all systems studied, the apparent  $D_{it}$  (density of interface states) changes when the top high-k material is modified. Another interesting phenomenon is revealed when different methods of  $D_{it}$  characterization are compared - each method points out a different high-k as the one with the lowest  $D_{it}$ . These observations imply that the C-V characteristics do not reflect only the role of Ge interface traps, but also of traps throughout the whole stack, at least to a distance of 2.7 nm (the total thickness of the passivation stack) from the Ge surface. These results emphasize even more the great challenges in integrating Ge as a new channel material. We have also analyzed the band alignment for all high-k dielectrics using XPS with respect to the underlying layers. All high-k dielectrics have similar band gaps at the range of 5.2-5.9 eV. The conductance and valence band offsets with respect to Ge are all larger than 1 eV, which make them all suitable for Ge-MOSFETs in terms of band alignment.

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Dawson, B.: TR+SE-WeM11, **7**  
de Rooij, M.R.: TR+BI-TuM5, 1  
Deram, M.: TR+SE-WeM10, 7  
Dugger, M.T.: LB+EM+GR+MN+TR-WeA1, 8

## — E —

Eigenfeld, N.: TR+SE-WeM10, 7  
Eizenberg, M.: LB+EM+GR+MN+TR-WeA12, **9**  
Elliman, R.G.: LB+EM+GR+MN+TR-WeA7, 8  
Elmquist, R.: LB+EM+GR+MN+TR-WeA10, 9  
Erdemir, A.: TR+BI-TuM9, **1**  
Eryilmaz, O.L.: TR+BI-TuM9, 1  
Ewin, J.J.: TR-TuA9, 3

## — F —

Fadida, S.: LB+EM+GR+MN+TR-WeA12, 9  
Flater, E.E.: TR+SE-WeM10, 7  
Flores, M.: TR-TuP6, **5**  
Fridmann, J.: LB+EM+GR+MN+TR-WeA7, **8**

## — G —

Garcia, S.: TR+BI-TuM5, 1  
Ghodssi, R.: TR-TuA11, 3  
Giasson, S.: TR-TuA4, 3  
Gila, B.: LB+EM+GR+MN+TR-WeA7, 8  
Gilley, K.: TR+SE-WeM5, **6**

## — H —

Hahn, D.W.: TR+SE-WeM9, 6  
Hanrahan, B.: TR-TuA11, 3

Harker, M.: LB+EM+GR+MN+TR-WeA3, 8  
Harris, K.L.: TR+SE-WeM9, **6**  
Hebard, A.F.: LB+EM+GR+MN+TR-WeA7, 8  
Hofmann, T.: LB+EM+GR+MN+TR-WeA10, 9  
Hu, J.J.: TR+SE-WeM1, 6  
Hu, Y.C.: LB+EM+GR+MN+TR-WeA8, 8  
Huerta, L.: TR-TuP6, 5  
Hultman, L.: TR+SE-WeM4, 6  
Huo, S.: TR+BI-TuM2, 1

## — I —

Imai, E.: TR-TuP2, 5  
Ishigami, M.: TR+SE-WeM11, 7  
Israelachvili, J.N.: TR-TuA4, 3

## — J —

Jackson, S.A.: TR+SE-WeM12, 7  
Jensen, B.D.: LB+EM+GR+MN+TR-WeA3, 8  
Jimenez, O.: TR-TuP6, 5  
Jones, K.: LB+EM+GR+MN+TR-WeA3, 8

## — K —

Kaufman Osborn, T.: LB+EM+GR+MN+TR-WeA11, 9  
Kent, T.J.: LB+EM+GR+MN+TR-WeA11, 9  
Kiantaj, K.: LB+EM+GR+MN+TR-WeA11, **9**  
Kim, S.H.: TR+BI-TuM11, **1**  
Kong, C.S.: TR+BI-TuM10, 1  
Kostov, K.: LB+EM+GR+MN+TR-WeA9, 9  
Krick, B.A.: TR+SE-WeM9, 6; TR-TuA3, **3**; TR-TuA9, 3  
Krim, J.: TR-TuA12, **4**  
Kristiansen, K.: TR-TuA4, **3**  
Kummel, A.C.: LB+EM+GR+MN+TR-WeA11, 9

## — L —

Lacovig, P.: LB+EM+GR+MN+TR-WeA9, 9  
Larciprete, R.: LB+EM+GR+MN+TR-WeA9, 9  
Lemaitre, M.: LB+EM+GR+MN+TR-WeA7, 8  
Li, L.J.: LB+EM+GR+MN+TR-WeA8, 8  
Liddiard, S.: LB+EM+GR+MN+TR-WeA3, 8  
Lin, D.: LB+EM+GR+MN+TR-WeA12, 9  
Lin, F.-Y.: TR+BI-TuM10, 1; TR-TuP1, **5**  
Lin, K.C.: LB+EM+GR+MN+TR-WeA8, 8  
Lince, J.R.: TR+SE-WeM12, 7  
Linn-Molin, E.: TR+SE-WeM10, 7  
Lizzit, S.: LB+EM+GR+MN+TR-WeA9, **9**  
Lodge, M.: TR+SE-WeM11, 7  
Lund, J.: LB+EM+GR+MN+TR-WeA3, 8

## — M —

Marchman, K.R.: TR+BI-TuM10, 1; TR-TuA3, 3  
Martinez de Olcoz Sainz, L.: TR+SE-WeM4, 6  
Matthews, O.: TR+SE-WeM10, 7  
Menzel, D.: LB+EM+GR+MN+TR-WeA9, 9  
Miller, J.B.: TR+SE-WeM4, 6  
Misra, S.: TR-TuA11, **3**  
Miura, T.: TR-TuP2, 5  
Miyamoto, J.: LB+EM+GR+MN+TR-WeA2, 8  
Muratore, C.: TR+SE-WeM1, 6

## — N —

Nadzeyka, A.: LB+EM+GR+MN+TR-WeA7, 8  
Nyns, L.: LB+EM+GR+MN+TR-WeA12, 9

## — P —

Pai, W.W.: LB+EM+GR+MN+TR-WeA8, **8**  
Pastewka, L.: TR-TuA1, 3  
Pei, L.: LB+EM+GR+MN+TR-WeA3, **8**  
Perry, S.S.: TR+BI-TuM2, 1; TR+SE-WeM5, 6; TR-TuA7, 3  
Phillpot, S.R.: TR+BI-TuM10, 1; TR-TuP1, 5  
Pitenis, A.A.: TR-TuA9, **3**  
Pluntze, A.M.: TR+SE-WeM12, 7  
Poda, A.: TR+SE-WeM10, 7  
Prasad, S.V.: LB+EM+GR+MN+TR-WeA1, 8

## — R —

Rajan, K.: TR+BI-TuM10, 1  
Real, M.: LB+EM+GR+MN+TR-WeA10, 9  
Ren, F.: LB+EM+GR+MN+TR-WeA7, 8  
Riddle, Y.: TR+SE-WeM5, 6  
Robbins, M.O.: TR-TuA1, **3**  
Rodriguez, E.: TR-TuP6, 5  
Rudy, A.: TR+BI-TuM2, 1

## — S —

Sawyer, W.G.: TR+BI-TuM10, 1; TR+SE-WeM9, 6; TR-TuA3, 3; TR-TuA9, 3  
Schubert, M.: LB+EM+GR+MN+TR-WeA10, 9  
Sharp, T.: TR-TuA1, 3  
Sinnott, S.B.: TR+BI-TuM10, **1**; TR-TuA3, 3; TR-TuP1, 5  
Sumiya, K.: TR-TuP3, 5  
Sun, X.: TR-TuP1, 5

## — T —

Tongay, S.: LB+EM+GR+MN+TR-WeA7, 8  
Tysoe, W.T.: TR+SE-WeM3, **6**  
Tzeng, Y.R.: LB+EM+GR+MN+TR-WeA8, 8

## — V —

Valefi, M.: TR+BI-TuM5, 1  
van der Zwaag, S.: TR+BI-TuM5, **1**  
Van Elshocht, S.: LB+EM+GR+MN+TR-WeA12, 9  
VanFleet, R.: LB+EM+GR+MN+TR-WeA3, 8  
Venkatachalam, D.K.: LB+EM+GR+MN+TR-WeA7, 8  
Voevodin, A.A.: TR+SE-WeM1, 6

## — W —

Wang, X.: LB+EM+GR+MN+TR-WeA7, 8

## — Y —

Yilmaz, D.E.: TR-TuP1, 5  
Yoshimura, M.: TR-TuP3, **5**

## — Z —

Zappe, M.: LB+EM+GR+MN+TR-WeA3, 8  
Zeng, H.: TR-TuA4, 3  
Zhao, X.: TR-TuA7, **3**  
Zufelt, K.: LB+EM+GR+MN+TR-WeA3, 8