Tribology Focus Topic
Room: 205 - Session TR+MN+NC-WeM

Surfaces and Interfaces in MEMS/NEMS
Moderator: J.A. Harrison, United States Naval Academy

8:00am **TR+MN+NC-WeM1 A Study of Au and Ru RF MEMS Contacts in Controlled Vacuum Environments**, ***M. Walker,*** North Carolina State University*, N. McGruer,* Northeastern University*, J. Krim*, North Carolina State University

Studies of RF MEMS switch performance under ultra clean and controlled environmental conditions have to date been extremely limited.[1] Such studies are highly valuable however, as they provide an opportunity to separately examine the impact of various factors such as contamination films, creep, deformation and stiction that plague current RF MEMS switch reliability. We have constructed a custom ultra high vacuum chamber with in situ surface cleaning, variable temperature and gas dosing capabilities in an effort to isolate the multiple variables that impact RF MEMS contact resistance and longevity. This chamber allows us to study switches in atmosphere followed by studies performed in the cleanest environment possible. We have investigated cantilever MEMS devices with both Au on Au and Ru on Ru contacts. Au on Au switches have so far been investigated by the vast majority of studies, and provide baseline material for our studies. Ru on Ru switches are far less studied. Ru is currently our material of interest on account of its harder properties that resists creep and deformation. In atmosphere we observe the resistance of a closed switch over time then open the switch. We pump the chamber to a base pressure of 9 x 10-10 torr followed by measuring the resistance over time then opening the switch. Surface cleaning is performed via in situ oxygen plasma. This is followed by closing the switch and observing the resistance over time. We have observed switches that have initially had infinite resistance in both atmosphere and UHV exhibit tens of ohms contact resistance after oxygen plasma cleaning. The resistance values after oxygen cleaning are closer to the theoretical values for clean contact. We compare these resistance changes to theoretical models[2] that account for creep and deformation of the switch contacts. A study of contact resistance as a function of hydrocarbon uptake is in progress.[3] This work was supported by the DARPA Center for RF MEMS Reliability and Design Fundamentals Grant # HR0011-06-1-0051 and the AFOSR Extreme Friction MURI Grant #FA9550-04-0381.

[1] C. Brown, A. Morris, A. Kingon, J. Krim, submitted to J. MEMS

[2] O. Rezvanian, C. Brown, M. Zikry, A. Kingon, J. Krim, D. Irving, D. Brenner, submitted to J. Applied Physics

[3] H. Koidl, W. Rieder, Q. Salzmann, vol. 22, No. 3, 1999 .

8:20am **TR+MN+NC-WeM2 Bimetallic Nanoparticles as Surface Coatings in MEMS Switch Contacts**, ***M.L. Jespersen***, Air Force Research Laboratories*, S.T. Patton,* University of Dayton Research Institute*, J. Slocik, R. Naik, A. Campbell, A.A. Voevodin*, Air Force Research Laboratories

Microelectromechanical systems (MEMS) switches have a broad range of applications in the aerospace, communications, and electronics industries. However, contact failure, especially during hot switching, prevents widespread implementation of the next generation MEMS devices in new technologies. Few studies have investigated physical and chemical processes that occur on modified MEMS contact interfaces, although one published study used self-assembled monolayers (SAMs) as a switch lubricant.[1] These SAMs thermally decompose in the contact.[1] We also have investigated nanoparticle liquids (NPLs) deposited onto MEMS contacts as nanomaterial-based lubricants, which improved the performance and durability of MEMS contact switches by orders of magnitude.[2] In this study, we investigated bimetallic (Au/Pd) nanoparticles (NPs) as surface lubricants for MEMS contact switches. Bimetallic systems offer enhanced properties for MEMS by taking advantage of the physical characteristics of the individual components. For example, Au has a low contact resistance, while Pd exhibits higher melting temperatures and lower adhesion. Performance of bimetallic NP-lubricated contact surfaces were investigated, using a micro/nanoadhesion apparatus as a MEMS switch simulator with in-situ monitoring of contact resistance and adhesion force. Ex-situ analyses of the chemical and physical processes at the contact interfaces were carried out using SEM, TEM, XPS, and scanning Auger spectroscopy. Bimetallic NPs exhibited orders of magnitude improvement in electrical performance and durability as compared to uncoated and SAM-coated contacts. The observed improvement in performance and reliability results from nanoscale surface roughness extending across multiple nanocontact regions, enhanced thermal and electrical conductivity over SAM coatings, and self-limited nanowire growth that prevents shorting failure in the contact regions, as determined from physical and chemical analyses. Based on these results, bimetallic nanoparticles are promising candidates as surface lubricants for MEMS switch contacts.

[1] S. T. Patton, K. C. Eapen, J. S. Zabinski, J. H. Sanders, and A. A. Voevodin, “Lubrication of MEMS RF switch contacts using self-assembled monolayers,” J. Appl. Phys., vol. 102, pp. 024903-1 – 024903-5, 2007.

[2] A. A. Voevodin, et al."Nanoparticle-Wetted Surfaces for Relays and Energy Transmission Contacts." Small, vol. 3, pp. 1957-1963, 2007.

8:40am **TR+MN+NC-WeM3 Contact Mechanics and Lubrication of MEMS Switches: Insights from Atomic and Multiscale Modeling**, ***D.W. Brenner***, North Carolina State University **INVITED**

We have been using a combination of molecular modeling and continuum analysis to understand and predict a range of dynamic processes that occur during the contact of RF and capacitive MEMS switches. The results of these studies are being used in the rational design of new materials and lubrication strategies for enhancing the lifetimes of these devices. In the case of closed RF-MEMS switches, it will be shown that the time-dependent resistance is well described by a power law, and using an asperity creep model that the prefactor and exponent in the power law can be related to the surface roughness and creep coefficient, respectively. For capacitive switches we have used molecular modeling to explore the efficacy of a “bound+mobile” lubrication scheme involving tricresylphosphate molecules diffusing on a octadecytrichlorine self-assembled monolayer. Temperature-dependent diffusion coefficients calculated from the simulations have been used in a scaling relation for liquid lubrication that depends on the ratio of the contact area to the product of the lubricant diffusion coefficient and the switch cycle time. This combination of atomic modeling and multiscale analysis predicts that this molecule-surface combination will only be effective for temperatures greater than ~200K and up to ~MHz oscillation frequencies.

This work was done in collaboration with D. Irving, O. Rezvanian, C. Brown, M. Zikry, A. Kingon, C. Padgett and J. Krim. This work was supported by the Extreme Friction MURI program, AFOSR grant FA9550-04-1-0381 and the Office of Naval Research.

9:20am **TR+MN+NC-WeM5 Sidewall Tribometer Study of Vapor Phase Lubricants for MEMS**, ***D.A. Hook****, B. Vlastakis, B.P. Miller,* North Carolina State University*, J. Rutledge,* University of California, Irvine*, M.T. Dugger*, Sandia National Laboratories*, J. Krim*, North Carolina State University

Long hydrocarbon and fluorocarbon based monolayers have been widely used in MEMS applications to prevent release related stiction and adhesion. These and similar monolayers, however, have proven ineffective as MEMS lubricants. Indeed, even the most robust of SAM layers fails to protect devices from tribological failure for either normal or sliding cyclic contact.[1] Alternate schemes, such as vapor phase lubrication, must therefore be developed if progress is to occur.[2] The vapor phase of pentanol has recently been reported by Seong et al to extend the lifetime of a MEMS device in a mixture of dry nitrogen and various concentrations of pentanol. Macroscale friction experiments have meanwhile shown the build up of long carbon chain reaction films in identical conditions.[3] In order to probe the effectiveness of pentanol and related alcohols, we have employed a ringdown measurement technique with a specially designed MEMS sidewall tribometer to compare the coefficients of friction of a device before and after introduction of pentanol into a vacuum chamber at one monolayer of coverage. Initial measurements show no change in the coefficient of friction, but subsequent measurements show a progressive decrease. This reflects a formation of a reaction film extremely quickly upon rubbing. Lifetime measurements using the sidewall tribometer were also taken with shorter chain alcohols, namely trifluoroethanol and ethanol, at one monolayer coverage to determine whether amount of carbon present affects the lubricating properties as well as the role of methyl versus trifluoromethyl termination. It has been found that ethanol’s ability to lubricate is dependant upon the initial state of the device whereas trifluoroethanol and pentanol will lubricate a device that has previously failed. Work funded by the AFOSR Extreme Friction MURI #FA9550-04-0381.

[1] Hook, D.A., Timpe, S.J., Dugger, M.T., Krim, J., “Tribological Degradation of Fluorocarbon Coated Silicon Microdevice Surfaces in Normal and Sliding Contact” Journal of Applied Physics, in press

[2] Krim, J., Abdelmaksoud, M., “Nanotribology of Vapor-Phase Lubricants” Tribology Issues and Opportunities in MEMS, B. Bhushan, ed. 1998 pp. 273-284

[3] Asay, D.B., Dugger, M.T., Ohlhausen, J.A., Kim, S.H., “Macro- to Nanoscale Wear Prevention via Molecular Adsorption”, Langmuir 2008, 24, 155-159.

9:40am **TR+MN+NC-WeM6 Effects of Organic Vapor Adsorption on Nanoasperity Adhesion and Friction – From Fundamentals to MEMS Applications**, ***S.H. Kim***, Pennsylvania State University

As the contact size involved in mechanical device operations decreases, the adsorption of gaseous molecules on the contact surface – which normally ignored in macroscopic measurements – becomes more important and dominant factors governing the contract properties such as adhesion and friction. Water adsorption can causes high adhesion and severe wear of silicon oxide surfaces. In contrast, alcohol vapor adsorption from the ambient can provide unprecedentedly efficient lubrication effects for operation of microelectromechanical systems (MEMS) with sliding contacts. Atomic force microscopy (AFM) is an ideal tool for studying the adhesion and frictional behavior of nanoscale asperity contacts. The tribological response of a silicon nanoasperity contact was studied with AFM with alcohol vapors as the VPL. Alcohol vapor adsorption on silicon oxide surface readily forms a thin organic film on the surface which mitigates the adhesion and friction forces between the AFM tip and substrate surfaces. The origin of adhesion and friction changes in the presence of alcohol vapor is elucidated through vibrational spectroscopic investigation of the thickness and structure of the adsorbed layers as well as theoretical calculations of their tribological responses.

10:40am **TR+MN+NC-WeM9 Dynamics and Spreading of Pentanol and Other Alcohols for MEMS Applications**, ***B.P. Miller***, *J. Krim*, North Carolina State University

Microelectromechanical Systems (MEMS) have the potential to revolutionize widespread technologies, but friction and other tribological issues are currently preventing commercialization of devices that contain surfaces in sliding contact. Self-assembled monolayers (SAMs), while highly effective against release related stiction, have proven ineffective as MEMS lubricants. Indeed, even the most robust of SAMs fail to protect devices from tribological failure for either normal or sliding cyclic contact.[1] Alternative MEMS lubrication schemes must therefore be developed if progress is to occur. Vapor phase lubrication has been proposed as a solution to the issue of tribological device failure in Micro-Electro-Mechanical Systems (MEMS) with TCP and alcohol vapors attracting much interest as candidate materials.[2] In an effort to understand the basic mechanisms of lubrication we have performed a quartz crystal microbalance (QCM) study of the uptake, sliding friction, and spreading rates of adsorbed ethanol, trifluoroethanol (TFE) and pentanol films on silicon, aluminum and perfluorodecyltrichlorosilane (PFTS) treated substrates.[3] In response to the oscillatory motion of the QCM, pentanol, and also ethanol, exhibit viscoelasticity and/or interfacial slippage when adsorbed on silicon or PFTS, implying that enhanced tribological performance may be expected in MEMS devices. TFE exhibited slippage on silicon but not PFTS. Significantly lower mobility levels were observed for all three alcohols adsorbed on aluminum. This work is funded by AFOSR Extreme Friction MURI Grant #FA9550-04-1-0381.

[1] D. A. Hook, M. T. Dugger, and J. Krim. J. Applied Physics, in press.

[2] J. Krim and M. Abdelmaksoud, in Tribology Issues and Opportunities in MEMS, B. Bhushan, ed. (Kluwer Academic, Dordrecht, 1998), pp. 273-284; W. Neeyakorn et al., Trib Lett. 27 (2007) 269-276; D. B. Asay, M. T. Dugger, S. H. Kim. Trib Lett. 29 (2008) 67-74.

[3] B.P. Miller and J. Krim, Submitted to Langmuir.

11:00am **TR+MN+NC-WeM10 Effect of Fluid Flow on the Sensitivity of Microcantilever Sensors**, ***R. Desikan***, *D. RangaPrasad, A. Passian, R.H. Datar, T.G. Thundat*, Oak Ridge National Laboratory

Microcantilever arrays are emerging as an attractive platform for detection of biomolecules because of their high sensitivity, miniature size, and their ability to work under solution. Selectivity in detection is accomplished by immobilizing receptor molecules on one surface of the cantilever. Interaction of biomolecules with the immobilized receptors results in cantilever bending. In general, the cantilevers are operated under constant flow of the buffer solution. Since cantilevers are sensitive to fluid flow, the flow rate is kept constant during injection of analytes in the flowing buffer solution. In some cases, reference cantilevers are used to eliminate the effect of fluid flow rate. However, we have observed that the interaction of analytes on receptors on cantilever surface is affected by the variations in the flow rate. More analyte molecules tend to bind the receptors on cantilever surface in static condition when molecular interaction is influenced by diffusion, compared to dynamic condition where analyte molecules flow across the cantilever using a flow control system. This work addresses the issues associated with biomolecular adsorption kinetics, flow rate dependence, and cantilever geometry for increasing the sensor sensitivity.

11:20am **TR+MN+NC-WeM11 Self-Affine Fractal Analysis of MEMS Surfaces for Minimizing Adhesion**, *D.-L. Liu,* Worcester Polytechnic Institute, *J. Martin,* Analog Devices Incorporated, ***N.A. Burnham***, Worcester Polytechnic Institute

Differing approaches to studies of the influence of surface roughness on adhesion have recently appeared in the literature. Molecular dynamics has been used to simulate the contact of two surfaces and found that atomic-scale roughness can have a large influence on adhesion, causing the breakdown of continuum mechanics models.[1] Yet a simple continuum model predicted the qualitative behavior of adhesion as a function of root-mean-square surface roughness in the nanometer to tens-of-nanometers range.[2] Although a useful first-order approximation, the assumptions in the latter work were severe; a more descriptive approach is necessary in order to design surfaces that either maximize or minimize adhesion. Self-affine fractal analysis provides a reasonable framework in which to move forward. In addition to the root-mean-square (RMS) roughness, it characterizes surfaces with two more parameters, the roughness exponent and the correlation length. A high roughness exponent and a small correlation length should minimize adhesion for two rough surfaces, as predicted by Chow.[3] Our adaptation of his work shows similar results for the case of a smooth tip of an atomic force microscope (AFM) and a rough surface. Specifically, the surfaces had the same RMS roughness, 0.2 µm, and the same lateral correlation length, 3.0 µm, but their roughness exponents ranged from 0.1 to 1.0. The height-height correlation functions and the height distribution functions were calculated from the surface height data, and the three fractal parameters were extracted for all the surfaces. The adhesion between a smooth AFM tip and the fractal rough surfaces were then calculated based on both the height distribution and the force-distance relationship between one molecule in the AFM tip and the fractal rough surface. The adhesion was found to decrease linearly as the roughness exponent increased. Furthermore, experimental data of the adhesion between AFM tips and MEMS surfaces as a function of the three fractal parameters will be shown and compared with the theoretical predictions. The work presented here should help minimize adhesion in future MEMS devices and progress the understanding of adhesion between the atomic- and macro-scale.

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

[2] D.-L. Liu, J. Martin, and N.A. Burnham, Appl. Phys. Lett. 91, 043107 (2007).

[3] T.S. Chow, Phys. Rev. Lett. 79, 1086 (1997).

Tribology Focus Topic
Room: 205 - Session TR+NS+EM+NC-WeA

Nanotribology and Nanomechanics
Moderator: S.J. Bull, Newcastle University, UK

1:40pm **TR+NS+EM+NC-WeA1 Frictional and Transverse Shear Forces as Probes of Disorder and Anisotropy in Organic Semiconductors**, ***G. Haugstad***, *V. Kalahari, C.D. Frisbie*, University of Minnesota **INVITED**

The condensed matter properties of conjugated organic systems are critically important to thin-film transistors for flexible electronics. As with conventional (inorganic) semiconductors, crystallinity is expected to strongly impact electronic transport. But unlike inorganic semiconductors, details of intermolecular coupling also are important. It is well known from friction force microscopy on alkane-chain films (self-assembled monolayers) that sliding friction is exceedingly sensitive to disorder and molecular coupling. Friction anisotropy also has been observed on Langmuir-Blodgett and liquid crystal films, as relates to the crystallographic axes and molecular packing. This suggests that nanotribological phenomenology can be targeted towards the analysis of crystalline organic systems whose principal technological application resides outside of tribology. Recently we discovered that the presence of defects in the form of line dislocations (revealed via etching) within a given micron-scale grain of pentacene correlates with elevated friction. Moreover we discovered that images of shear force transverse to the fast-scan axis reveal the crystallographic orientation of pentacene grains.[1] We report more detailed investigations into these novel tribological phenomena, expanded to additional conjugated crystalline organic thin films as well as surfaces of bulk single crystals. We also broaden our methodology to include shear modulation force microscopy, to isolate purely elastic effects under a pinned contact from dissipative effects under a sliding contact. We compare tribological/nanomechanical observations of crystal anisotropy to electronic transport measurements, uncovering systematic relationships. Our findings establish a highly reproducible phenomenology across a family of similar systems, but with some interesting differences related to crystal structure. We expect these findings to be important to both electronic transport in organic thin-film semiconductors and to the fundamentals of tribology on crystalline organic systems.

[1] K. Puntambekar, J. Dong, G. Haugstad and C. D. Frisbie, Adv. Funct. Mater. 16, 879 (2006).

2:20pm **TR+NS+EM+NC-WeA3 Load Dependence of Interfacial Friction Analyzed by Nanoparticle Manipulation**, ***D. Dietzel***, University of Muenster and Forschungszentrum Karlsruhe, Germany, *A. Schirmeisen*, University of Muenster, Germany

By analyzing the friction between an atomic force microscopy (AFM) cantilever tip and the sample surface, friction force microscopy (FFM) has proven to be a powerful tool for nanotribology. Unfortunately, FFM has some limitations inherent to the experimental configuration. For example it is extremely difficult to measure friction as a function of the normal force applied to the interface, since any quantitative interpretation is complicated by the simultaneous variation of the contact area. In order to address the important problem of load dependence of nanoscale friction, a technique for measurements under well defined interface conditions is required. Well-defined interfaces can be investigated by friction force analysis during nanoparticle manipulation.[1] However, the aspect of load dependence can not be analyzed as long as the cantilever is just pushing the particles from the side. In this work, a new approach for load dependent friction measurements by particle manipulation is presented. The AFM tip is used for pushing the nanoparticle while exerting a defined normal force simultaneously. For this approach the AFM-tip is centered on top of a highly mobile nanoparticle. Depending on the scanning conditions, the tip is either scanned on top of the particle or the particle moves together with the tip on the surface. In the latter case, the cantilever torsion during particle movement represents the interfacial friction between particle and surface. Thermally evaporated Sb-islands on HOPG substrate were used as a model system for the manipulation experiments. To ensure clean interface conditions and high mobility of the particles, all measurements have been performed under UHV conditions. When scanning the tip on top of the Sb-particle, the cantilever normal force is used to control the manipulation. Low normal forces usually result in scanning the tip on top of the particle, whereas higher normal forces can overcome the particle's static friction and induce the switch to simultaneously moving the particle with the tip. Once the particle is moving, the normal force can be further increased, making load dependent friction measurements possible. In contrast to conventional FFM, the measured friction originates from a well defined interface of constant size and can thus unambiguously be interpreted with respect to the load dependence of the interfacial shear stress.

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

2:40pm **TR+NS+EM+NC-WeA4 Atomistic Simulations of Tribology at Sliding Surfaces**, *P. Barry, P. Chiu, T. Liang, S.S. Perry, W.G. Sawyer, S.R. Phillpot,* ***S.B. Sinnott***, University of Florida

Friction is of tremendous technological importance and has, consequently, been under study for centuries. This research has led to the development of classical theories of friction that have successfully solved several tribological problems. However, these classical theories do less well at describing the behavior of advanced materials that operate under extreme environments. Here, we describe integrated experimental and computational studies of atomic-scale friction and wear at solid-solid interfaces across length and time scales. The influence of molecular orientation in the case of polymer films of polytetrafluoroethylene and polyethylene, on friction and wear are discussed. In addition, the tribological behavior of polycrystalline molybdenum disulfide is elucidated in a combination of atomic-force microscopy and classical molecular dynamics simulations. These results provide new insights into how classical theories of friction may be modified to better describe advanced materials under extreme environments. This work is supported by a MURI from the Air Force Office of Scientific Research through grant FA9550-04-1-0367.

3:00pm **TR+NS+EM+NC-WeA5 Local Thermomechanical Characterization of Phase Transitions in Polymers using Band Excitation Atomic Force Acoustic Microscopy with Heated Probe**, *M.P. Nikiforov,* ***S. Jesse***, Oak Ridge National Laboratory, *L. Germinario*, Eastman Kodak, *S.V. Kalinin*, Oak Ridge National Laboratory

Nanoscale confinement effects strongly affect thermomechanical properties of materials and composites, including surface- and interface-induced changes in melting and glass temperatures, temperature-dependent interface bonding, and local viscoelastic properties. Probing these behaviors locally overcomes the challenge of non-destructive characterization of thermomechanical behaviors in small volumes. Here we demonstrated that phase transitions in polymeric materials induced by the heated probe can be detected by band excitation acoustic force microscopy. Phase transition can be detected using any of the 3 independently determined parameters, such as oscillation amplitude, resonance frequency, and Q factor. Glass transition as well as melting in polymers can be efficiently differentiated using this technique. We developed the heating protocol to maintain contact area and effective force constant during the heating cycle, thus allowing for reproducible measurements and potentially for quantitative extraction of local thermomechnical properties. The contact mechanics models for tip indenting the surface are discussed. These models provide a framework connecting viscoelastic properties of the surface and oscillation parameters measured in the experiment. Currently, the major limitation of thermal probe techniques, such as Wollastone probe, is large indentation footprint (~ 10 um) of the probe on the surface after the experiment. Our method overcomes this problem. In the best case scenario, development of the band excitation acoustic force microscopy combined with a heated-probe approach will provide us a tool for non-destructive measurements of the glass transition and melting temperatures with sub-100 nm spatial resolution. Research was sponsored by the Center for Nanophase Materials Sciences, Office of Basic Energy Sciences, U.S. Department of Energy with Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC.

4:00pm **TR+NS+EM+NC-WeA8 Effects of Structure, Doping, & Environment on the Tribochemistry of DLC**, ***J.A. Harrison***, *J.D. Schall, G. Gao, M.T. Knippenberg, P.T. Mikulski*, United States Naval Academy

The classical reactive empirical bond-order potentials have been used to model a wide range physical and chemical processes in covalent materials. Despite the many successes of these potentials, they are not able to model all properties of materials equally well nor are they able to model systems where intermolecular interactions are important. For hydrocarbons, intermolecular forces can be modeled using an adaptive algorithm as is used in the AIREBO potential. We will briefly discuss our recent efforts to add additional elements, such as Si, to the second-generation REBO formalism, thereby extending the types of materials which can be modeled with these potentials. In addition, we will also briefly discuss the parameterization of additional atom types for the AIREBO formalism. The majority of the talk will focus on recent simulations that have examined atomic-scale friction and wear of diamondlike carbon (DLC) and doped DLC. Work supported by The Office of Naval Research and The Air Force Office of Scientific Research as part of the Extreme Friction MURI & the Tribology Program.

4:20pm **TR+NS+EM+NC-WeA9 Low-Wear Variable-Slope Method of Lateral Force Calibration**, ***S. Chakraborty****, D. Eggiman, C. DeGraf, K. Stevens, D.-L. Liu, N.A. Burnham*, Worcester Polytechnic Institute

Dozens of publications address the confounding problem of lateral force calibration. The existing techniques suffer from limitations including: i) repeated measurements are necessary, thereby causing wear to the tip, ii) calibration is done on another cantilever other than the one that will be used in the experiment, iii) specialized or expensive equipment is required, iv) the method is time consuming, v) the calibration is performed ex-situ, vi) a form for the frictional dependence on load is assumed, and vii) the equilibrium diagrams of the forces acting on the tip are incorrect. We describe a method[1,2] that overcomes all of these problems; it uses an easily available test sample with a continuously variable slope. The theory and proof-of-concept experimental data will be shown. If confirmed as a robust approach, lateral forces will at last be tamed by simple, quick, and potentially accurate calibration.

[1] D. Eggimand, senior thesis, Physics Department, Worcester Polytechnic Institute, 2007.

[2] C. DeGraf and K. Stevens, senior thesis, Physics Department, Worcester Polytechnic Institute, 2006.

4:40pm **TR+NS+EM+NC-WeA10 The Effect of Tip Size on Frictional Forces in Self-Assembled Monolayers**, ***M.T. Knippenberg***, United States Naval Academy

Molecular dynamics simulations have been used to investigate the differences in molecular forces between a nominally flat tip, which is infinite in extent, and a spherical tip when both tips are in sliding contact with a self-assembled monolayer. The simulation technique used provides a method for evaluating contact forces of individual atoms, which are defined as the force between single atoms and the sliding tip. From this, atoms can be described as either contributing forces that push the tip forward, or resist the forward movement of the tip. Multiple loads are applied to both tip shapes during sliding, providing the opportunity to investigate force propagation as a dependence on load. Additionally, geometrical information such as the occurrence of gauche defects during sliding is investigated.

5:00pm **TR+NS+EM+NC-WeA11 Microscale Tribology of Nanostructured Coatings**, ***K.J. Wahl****,* U.S. Naval Research Laboratory*, E. So,* U.S. Naval Research Laboratory and PSU*, M.C. Demirel*, Pennsylvania State University

Novel nanostructured architectures are being explored for a wide range of applications including mimicking bioadhesive pads on insects and geckos, RF-microelectronics switches with robust compliant carbon nanotube films, and energy harvesting from friction by rubbing nanostructured piezoelectric coated fibers together. Developing an understanding of how these collections of nanostructured materials behave collectively requires experimental approaches at micron length scales. Experimental examination of the mechanics and tribology of materials in this intermediate regime can be influenced by macroscale phenomena (such as wear and interfacial transfer film formation during sliding) as well as phenomena more often associated with nanoscale contacts (such as significant adhesion contributions). In this talk, we will present tribological and mechanical analysis of columnar nanostructured poly-(p-xylylene) (PPX) thin films. Experiments are performed using nanoindentation and microtribology tools to examine the effects of load, counterface material, roughness, and transfer film formation on microscale tribological response. The PPX films are structurally anisotropic, consisting of nanowires oriented at various angles with respect to the surface normal. Sliding friction experiments performed at discrete angles with respect to the nanowire orientation resulted in relatively uniform friction behavior but significant differences in deformation response of the films. A simple mechanical model is proposed to explain the observed depth anisotropy. The value of monitoring both friction and contact depth simultaneously will be discussed and evaluated in context of materials exhibiting highly anisotropic mechanical properties.

5:20pm **TR+NS+EM+NC-WeA12 Characterization of the Al/Si Interfaces under Dry Wear Conditions**, ***J.F. Su****, X. Nie, V. Stoilov*, University of Windsor, Canada

Plastic deformation and damage accumulation at the contact surface are two important aspects of sliding wear of metal-matrix composite(MMC) materials such as AlSi alloys. The particular topography of the surfaces of the AlSi alloys has triggered the idea that the silicon particles form a load-bearing surface over which the counter surfaces are sliding. Therefore the wear resistance of AlSi surface is thought to originate from the high hardness of the silicon surface formed by the primary Si particles(inclusions). On the other hand the mechanical strength of the reinforcement(Si)/matrix(Al) interface in a MMC is the primary factor determining the strength on the load bearing Si formation. In this work we have developed a hybrid method to characterize the interface strength of an MMC, combining a nano/micro indentation experiment and an atomistic analysis. The nano/micro indentation experiment was carried out by indenting individual reinforcement particles on a free surface with a nano/microindenter. The dependence of indentation response on the interface properties was systematically studied and the interface strength was extracted from the threshold stress for the sink-in of the Si particles. With this method, the shear strength of an Al/Si interface was measured approximately 330MPa which compares well with the lower bound of an atomistic simulation with a modified embedded atom method (MEAM) potential.

Thursday Morning, October 23, 2008

In Situ Microscopy and Spectroscopy: Interfacial and Nanoscale Science Topical Conference
Room: 310 - Session IS+NS+TR+NC-ThM

In Situ Spectroscopy – Dynamic Nanoscale Processes
Moderator: S. Kodambaka, University of California, Los Angeles

8:00am **IS+NS+TR+NC-ThM1 Spatially-Resolved, Surface-Species Concentrations from Electron Reflectivity -- How Graphene Grows on a Metal**, ***K.F. McCarty**, E. Loginova, P.J. Feibelman, N.C. Bartelt*, Sandia National Laboratories

The rates of many surface processes, and notably of film growth, are governed by the concentrations of mobile adsorbed species. But, few techniques, if any, are available to measure small concentrations of adsorbed species with high spatial resolution. Therefore, the relationship between adsorbates and surface processes typically emerges from indirect observations. Motivated by this limitation, we are developing a technique based on electron reflectivity to obtain local adsorbate concentrations. We measure electron reflectivity changes from the brightness of low-energy electron microscopy (LEEM) images. They yield the local surface-species concentration with high spatial and temporal resolution. This quantitative approach offers the ability to determine the local adsorbate concentrations on heterogeneous surfaces dynamically and under in-situ conditions. We will illustrate the technique's capability with a direct determination of the relationship between mobile carbon adatoms, and the growth of graphene (i.e., of single atomic sheets of graphitic carbon) on Ru(0001), a representative metal. The carbon is supplied by segregation from the bulk metal upon cooling, or by deposition from an evaporator. We find that the reflectivity of low-energy electrons decreases in strict proportion to the concentration of adsorbed, gas-like carbon. By calibrating using known coverages, we can determine absolute adatom concentrations. The graphene growth mechanism was deciphered by simultaneously measuring the instantaneous growth rate of individual graphene islands, and the concentration of surrounding carbon adatoms. The mechanism is very striking and in sharp contrast to metal epitaxy. We found that: the graphene growth rate is limited by carbon atom attachment and not by carbon atom diffusion; the growth rate as a function of supersaturation is highly nonlinear. We will present a model that explains these observations and provides insight into the molecular processes by which graphene grows. Separately, we have determined the carbon adatom concentrations that are in equilibrium with the carbon in Ru's bulk and with graphene, respectively. This information helps understand the competition between the system's three possible carbon configurations: C in bulk Ru, C as adatoms, and C in graphene. This research was supported by the Office of Basic Energy Sciences, Division of Materials Sciences, U. S. Department of Energy under Contract No. DE-AC04-94AL85000.

8:20am **IS+NS+TR+NC-ThM2 Electron Diffraction Characterization of In Situ Deformation of Gallium Oxide Nanobelts**, ***J.M. Vaughn**, M.E. Kordesch*, Ohio University

A transmission electron microscope fitted with a home-built nano manipulator for in situ mechanical deformation of nanobelts is reported. Nanobelts of beta Ga2O3 are grown by the vapor transport method from gallium metal in an argon gas flow at 950 degrees centigrade. A single 2.5 um wide, approximately 200 nm thick and 10's of microns long belt is deformed by direct contact with the manipulator probe. Deflections of up to 180 degrees are possible without fracture of the belt. A series of TEM diffraction patterns are collected during belt deformation. The diffraction pattern is observed to distort as the belt is deformed. In addition to the distortion of the monoclinic belt diffraction pattern, additional diffraction spots are observed through belt deformation. Analysis of the additional spots and deflection in preexisting spots reveal simultaneous lengthening and contracting in measured planar spacings. This data is modeled by lattice deformations, which allows for such a large deformation of the belt. The lattice deformation model results in the lattice constant 'c' having two simultaneous values for any given diffraction pattern. The maximum simultaneous deformation in 'c' is measured to be 11.3 and 16.3 Angstroms. Lattice constant 'a' behaves similarly with values 5.1 and 7.9 Angstroms. Finally, the lattice deformation model is compared to a plane slipping model, which may also explain the additional spots and deformation.

Funded by a 2005 AVS Undergraduate Research Award.

8:40am **IS+NS+TR+NC-ThM3 Direct Observation of Carbon Nanotubes Formation from Selectively Fabricated Catalyst Particles**, ***R. Sharma***, Arizona State University **INVITED**

Carbon nanotubes (CNT) have many advantageous properties with potential for diverse advanced materials applications if their controlled synthesis can be optimized. For some applications, such as field-emitting displays, in-situ deposition of catalyst particles is an important step for CNT synthesis. Post synthesis characterization of CNTs is frequently performed using transmission electron microscopy (TEM) techniques. Therefore environmental scanning transmission electron microscope (ESTEM) is perfectly suited for in situ observations of nucleation and growth of CNTs. A modern ESTEM, equipped with a field-emission gun (FEG), energy filter or electron energy loss spectrometer, scanning transmission electron microscopy (STEM) coils, and bright and dark field detectors, is a versatile tool for understanding their synthesis process at nanometer level. We have employed a modified Tecnai-F20 ESTEM to understand the catalytic chemical vapor deposition process for CNT synthesis. Time, temperature and pressure resolved digital video imaging is used to determine the effect of synthesis condition on their structure and morphology. Statistical analysis of the CNTs formed under varying synthesis conditions show that 95% yield for SWCNTs can be achieved at 650oC in 1 mTorr of acetylene using Ni as catalyst. We have combined electron beam induced decomposition (EBID) of nonacarbonyl diiron (Fe2(CO)9) to fabricate arrays of Fe particles that are catalytically active for the thermal decomposition of acetylene to form multiwall CNTs. Atomic resolution video images are used to understand the nucleation and growth mechanism from crystalline catalyst particles. Detailed phase transformation of the catalyst particle and CNT growth mechanisms from selectively fabricated Fe particles will be presented.

9:20am **IS+NS+TR+NC-ThM5 Investigating Catalyst Behavior Prior to and during the Growth of Carbon Nanotubes with Environmental Cell TEM**, ***E.A. Stach**, S.M. Kim, D.N. Zakharov, P. Amama, C. Pint, R.H. Hauge, B. Maruyama*, Purdue University **INVITED**

In order to understand how carbon nanotubes form, one must have a detailed understanding of the size, shape and evolution of the catalysts responsible for their nucleation and growth. In this presentation, we describe our recent studies in understanding the evolution of Fe catalysts deposited on alumina during the so-called supergrowth of carbon nanotubes. These studies rely heavily on the exploitation of the unique capabilities of environmental transmission electron microscopy to observe at the atomistic scale how catalyst nanoparticles transform under varying regimes of temperature and pressure. We will show that modifications of the substrate treatment and carrier gas atmosphere have a strong effect on catalyst coarsening. In particular, we find the presence of H2O – the key ingredient in supergrowth – leads to a reduction in the Ostwald ripening of the Fe catalysts, thereby leading to denser nanotube carpets. Additionally, under conditions identical to those used in supergrowth, we confirm the diffusion of Fe into the Al2O3 supporting layer. This effect could play a significant role in the catalyst surface density during supergrowth, as well as provide another route in which carpet growth may terminate. These studies are correlated with real time TEM observations of the Ostwald ripening rate of Fe nanoparticles on different supports in H2 and H2 + H2O atmospheres, and on the nucleation and growth of the tubes themselves.

10:40am **IS+NS+TR+NC-ThM9 The Large Chamber SEM: A New Tool for Non-Destructive Testing**, ***M. Klein***, VisiTec Microtechnik GmbH Germany

Although conventional SEMs are limiting the size of objects or production equipment to be inspected scanning-electron-microscopes (SEM) are well known instruments for the use in nearly any micro¬technology. A more flexible tool to allow a visual control of micro¬mechanical manu¬facturing, assembling, and testing process is not yet described. Analyzing human behaviour during the visual investigation of objects and adapting this behaviour, lead to a new concept of electron microscopes called Large Chamber Scanning Electron Microscope (LC-SEM) In this case the electron optics is installed within the vacuum chamber and can be positioned freely inside this chamber. This change of kinematics combines conventional SEM´s advantages of high resolution and high depth of focus with the possibility to observe and test micro¬mechanical handling and assembly equipment. Using the LC-SEM allows a new understanding of these processes. The paper describes development, functionality, and applications of this LC-SEM. There are fields of application within the microtechnology and macro¬technology as well. The paper is focused on the use of the LC-SEM within microtechnology, microassembly and micromecha¬tronics. For nearly any process of manufacturing in the microworld a transmission of information to the human macroworld is necessary. For this purpose especially a visual control is important. Optical microscopes are of limited use due to their small magnification and depth of focus (e.g. an optical microscope offers just a depth of focus of 2 µm at an enlargement of 100). Conventional scanning-electron-microscopes (SEM) offer a much better resolution and a better depth of focus but are limited in the size and weight of objects to be inspected because of the usually small vacuum-chambers. Conventional goniometer tables are constructed with a very high precision and for a load carrying capacity up to 20 kg. The load carrying capacity is greatly restricted in that in conventional goniometer tables it is necessary to provide numerous moving guide elements and slide carriages, which for cost reasons are only designed for a moderate load. Therefore an Large Chamber- Scanning Electron Microscope as a tool to support the investigation of microproduction has been developed which opens new fields of application to electron microscopy. Key to the functionality of this microscope is the adaption of human behaviour during the investigation of objects.

11:00am **IS+NS+TR+NC-ThM10 In-situ Electron Microscopy and Spectroscopy Studies of Interfaces in Advanced Li-ion Batteries under Dynamic Operation Conditions**, ***C.M. Wang***, *Z.G. Yang, S. Thevuthasan, J. Liu, D.R. Baer,* Pacific Northwest National Laboratory*, N. Salmon*, Hummingbirds Scientific

Repeated charging and discharging of a Li-ion battery induces microstructural evolutions both at the interface between the electrolyte and the electrode and within the electrode (active materials) due to Li migration. Although it has been established that this structural evolution is responsible for the failure of such batteries, the mechanisms of the microstructural evolution as a function of charging/discharging are not well understood. Advanced diagnostic tools such as electron microscopy along with other surface and bulk sensitive tools, usually in ex-situ mode, have been used to probe into this scientific issue. However, it has been realized that characterizing this interface using an ex-situ capability is a challenge as the materials will be altered during sample preparation and processing and the interface will be stable only under the operating conditions. In-situ capabilities that enable the observation of the structural and chemical changes during the dynamic operation of battery are needed to address this scientific and technological challenge. We have been developing an environmental holder capability for TEM, trying to gain fundamental scientific understanding of the chemical and structural evolution at the interface between the electrolyte and the electrode as well as within the electrodes under the dynamic operation conditions of the Li battery system. In the preliminary research work, we have explored the interface change using TiO2 nanowire as the anode material. Transmission electron microscopy (TEM) imaging, electron diffraction, and electron energy-loss spectroscopy (EELS) were used to probe into these structural evolutions during the operation of the battery.

11:20am **IS+NS+TR+NC-ThM11 The Dynamics of the Initial Oxidation Stages of Cu and Cu Alloys**, ***J.C. Yang***, University of Pittsburgh **INVITED**

Surface oxidation processes play critical roles in environmental stability, high temperature corrosion, electrochemistry, catalytic reactions, gate oxides and thin film growth as well as fuel reactions. Much is known about oxygen interaction with metal surfaces and about the macroscopic growth of thermodynamically stable oxides. At present, the transient stages of oxidation − from the nucleation of the metal oxide to the formation of the thermodynamically stable oxide − represent a scientifically challenging and technologically important terra incognito. Furthermore, since environmental stability is an essential property of most engineered materials, many theories exist to explain its mechanisms. However, nearly all classical theories assume a uniform growing film, where structural changes are not considered because of the previous lack of experimental methods to visualize this non-uniform growth under conditions that allowed for highly controlled surfaces and impurities. One can now see structural changes under controlled surface conditions, by in situ ultra-high vacuum transmission electron microscopy (UHV-TEM), and thereby challenge the commonly used assumption of a uniform oxide formation. Here, we present a systematic study of the dynamics of the initial and transient oxidation stages of a metal and alloys with in situ UHV-TEM. We have previously demonstrated that the formation of epitaxial Cu2O islands during the transient oxidation of Cu(100), (110) and (111) films bear a striking resemblance to heteroepitaxy, where the initial stages of growth are dominated by oxygen surface diffusion and strain impacts the evolution of the oxide morphologies. We are presently investigating the early stages of oxidation of Cu-Au and Cu-Ni as a function of oxygen partial pressures, temperatures and composition. For Cu-Au oxidation, the oxidation mechanisms change due to the limited Cu around the oxide island leading to a dendritic growth of the Cu2O islands. For Cu-Ni oxidation, the addition of Ni causes the formation Cu2O and/or NiO where the oxide type(s) and the relative orientation with the film depend on the Ni concentration, oxygen partial pressure and temperature. This research program is funded by the National Science Foundation (DMR 0706171) and Department of Energy (DE-FG02-07ER46446).

Tribology Focus Topic
Room: 205 - Session TR+SE+TF-ThM

Advances in Surface Engineering for Friction and Wear Control
Moderator: K.J. Wahl, U.S. Naval Research Laboratory

8:00am **TR+SE+TF-ThM1 Evaluation of Ti-In-N Films for Tribological Applications**, ***J.E. Krzanowski****, M. Nowicki*, University of New Hampshire

Titanium nitride and indium have both found applications as tribological coatings. While TiN is used primarily for its high hardness and wear resistance, indium can be used as a solid lubricant layer. In this study, we have examined the concept of using co-deposited TiN-In films for tribological applications. Ti-In-N films have been deposited by RF co-sputtering of Ti and In in a nitrogen/argon atmosphere. By varying the power to the Ti and In sources, the In/Ti ratio in the film was varied. Films were deposited at DC substrate bias levels of -50V and -150V. In both cases, as the In/Ti power ratio was increased, the indium content increased, but in a highly non-linear manner. At lower power ratios, the films had a cubic TiN structure, but as the power ratio increased, there was an abrupt transition to a hexagonal structure. Near the transition point, the films could also be amorphous, depending on film thickness, and thicker films were more likely to be crystalline. Below the transition point, the film composition depended strongly on substrate bias, and films deposited at -150V bias exhibited significantly reduced indium contents. Tribolgical tests were conducted using a pin-on-disk test with an alumina counterface. Most films showed shorter wear lives compared to TiN alone. The friction coefficients were found to depend on the In content in the films, and it was also found that heating films for short times in the range of 100-250C reduced friction coefficients.

8:20am **TR+SE+TF-ThM2 Nanostructured Sulfur Doped CHx-TiB2 Coatings for Improved Mechnical and Friction Performance**, ***B. Zhao***, *Y.W. Chung*, Northwestern University

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

8:40am **TR+SE+TF-ThM3 Latest Developments on the Family of C-alloyed TMD Self-lubricating Coatings**, ***A. Cavaleiro,*** SEG-CEMUC - University of Coimbra, Portugal*, T. Polcar,* CTU Prague, Czech Republik, *M. Evaristo*, SEG-CEMUC - University of Coimbra, Portugal **INVITED**

Due to their layered structure and weak inter-layer bonding, transition metal dichalcogenides (TMD) exhibit very interesting physical and tribological properties. Among different TMD families (TmS2, TmSe2 and TmTe2, with Tm = Mo, W, Nb) MoS2 and WS2 have been the most intensively studied in last decades. They are now currently used either as oil additives or as thin self-lubricating coatings. The industrial applicability of these coatings is still very limited owing to their two main drawbacks: (1) the loss of the tribological performance in humidity-containing environments and, (2) the low load bearing capacity. Several solutions have been proposed to overcome these problems as, for example, alloying TMD coatings with other elements or compounds, such as C, Ti, Pb, and TiN. The concept of coatings based on TMDs alloyed with carbon was introduced in the 90´s and was based on the expected synergy between the excellent frictional behavior of TMD in vacuum/dry air and the tribological performance of C-based materials. Improved frictional performance of the W-S-C coatings could be achieved when the coatings were tested by environmental cycling from dry to humid air (FC - friction coefficient from 0.02 to 0.15). Successive changes in the sliding mechanisms based on the modification of the contact layers were assigned as responsible for this behaviour. The TMD+C solution was adopted by the authors for their research by studying its extension to other TMD-C systems. The aim of this talk was to present the latest developments achieved within TMD-C magnetron sputtering deposited coatings concerning di-selenides (Mo-Se-C and W-Se-C). Lower friction coefficient was achieved in comparison to previous deposited W-S-C coatings, particularly in humid air. FC was possible to be kept lower than 0.05 in all testing conditions. Tests were performed with contact stress as high as 1.5 GPa without destruction of the coating. The frictional and wear mechanisms under different operating conditions were studied by nanoscale analysis of the wear tracks. The tribological performance, whatever the testing conditions, was attributed to the formation of a thin tribolayer consisting exclusively of TMD platelets with the (002) plans oriented parallel to the sliding motion. C is removed from the contact area during the re-orientaion process, only playing a secondary role by increasing the coatings density, avoiding surface oxidation and improving the loading bearing capacity.

9:20am **TR+SE+TF-ThM5 Reduction in Friction and Micropitting by Coatings and Lubricants Containing Inorganic Fullerenes**, ***S.J. Bull***, *A. Oila*, Newcastle University, UK

Improvement in component performance by reduction in friction and wear has been the focus of considerable research over the last forty years. As products become more highly engineered and component size is reduced the significance of friction and wear is increased, particularly in terms of improvements in energy efficiency, and the need to develop materials with improved triboloigcal performance becomes critical. Nanostructured materials are one way whereby this might be achieved. Recent work has focussed on the development and assessment of nanomaterials and composites for triboloigcal performance. In particular, the use of inorganic fullerene-like materials in the form of coatings and nanoparticles (and as the reinforcement for nanocomposites) has shown a lot of promise for tribological applications. This talk will highlight the use of inorganic fullerene nanoparticles as additives for lubricating oils or coatings to achieve a significant increase in the operational life of rolling/sliding components such as gears.

9:40am **TR+SE+TF-ThM6 Tribology of Carbon Films in Hydrogen and Deuterium Gas Environments**, *A. Erdemir*, ***O.L. Eryilmaz***, Argonne National Laboratory

Recent systematic studies in our laboratory have shown that certain diamond-like carbon (DLC) films are able to achieve superlow friction and wear when tested in hydrogen-containing test environments. In the presence of deuterium, we were also able to achieve very low friction and wear on these films. In this study, we used a combination of controlled-environment atmospheric pressure and vacuum tribometers to further verify the critical effects of hydrogen and deuterium on friction and wear of such films; then we used imaging SIMS and XPS methods to ascertain the near surface chemistry of their sliding surfaces. The combined results of tribological tests and surface analytical studies revealed that there exist a close correlation between the chemical nature of sliding DLC surfaces and their friction and wear behaviour. Specifically, we found that in the presence of both hydrogen and deuterium, the sliding contact areas of carbon films were covered by a hydrogen and deuterium film (only a few Å thick). The wear rates and friction coefficients are much higher if tests were run in dry nitrogen or vacuum than in hydrogen and deuterium. Overall, we show that superlow friction behaviour of certain DLC films is largely controlled by gas-surface interactions.

10:40am **TR+SE+TF-ThM9 Tribomaterials for Spacecraft: Testing & Surface Chemistry**, ***J.R. Lince***, The Aerospace Corporation **INVITED**

The spacecraft environment is challenging for tribocoatings and lubricants used in devices in satellites and launch vehicles. Areas of concern include vibration during launch, thermal cycling on orbit, and the need to work effectively for missions up to twenty years in duration without lubricant replenishment. Especially challenging is the need for tribomaterials to withstand the vacuum of space during lengthy missions. Spacecraft tribomaterials must exhibit low vapor pressures, since evaporation of lubricants can result in loss from and premature failure of devices, as well as contamination of sensitive spacecraft components. A relatively small set of liquid lubricants meet the vapor pressure requirement – while also meeting performance requirements for current spacecraft applications – including synthetic hydrocarbons and perfluorinated polyalkylethers. Soft solid lubricants such as molybdenum disulfide (MoS_2) and polytetrafluoroethylene (PTFE) have been used traditionally. More recently, hard low friction coatings such as hydrogenated diamond-like carbon have shown promise for operation in vacuum with existing spacecraft lubricants, or even unlubricated operation in vacuum. These solid- and liquid-based tribomaterials show performance in vacuum that differs with that in air, nitrogen, or even with small partial pressures of oxygen and water. This is especially important for spacecraft hardware, because it is often prohibitive to test them in a space-like environment, including vacuum, before launch. As such, differences between non-vacuum and vacuum testing need to be understood in order to predict how lubricated devices will perform in space. This talk will focus on a series of recent studies done at The Aerospace Corporation that elucidate the effects of vacuum and other environments on the tribological performance of several important spacecraft tribomaterials. The emphasis will be on how varying environments affect the surface chemistry of the materials.

11:20am **TR+SE+TF-ThM11 Nano-Smooth Diamond Coatings on Various Alloys for Ultralow Friction in the Presence of OH-Containing Lubricants**, ***T. Gries***, CNRS - ICARE, France, *C. Matta, M.I. De Barros Bouchet, B. Vacher*, Ecole Centrale de Lyon, France, *S. de Persis*, ICARE - CNRS, France, *L. Vandenbulcke*, CNRS, France

Titanium alloys and titanium-coated alloys are important materials for aerospace, mechanical, chemical and biomedical applications; however their applications could be extended by improving their tribological behaviour. This can be done by using diamond-based coatings which are outstanding materials for changing their surface properties. We have shown that nano-smooth fine-grained diamond coatings could be deposited on these alloys at moderate temperature, equal to or lower than 600°C, from CH_4-CO_2 species. They are in fact duplex coatings with an external diamond film, a titanium carbide sub-layer and a diffusion solid-solution. These coatings exhibit particularly strong adherence with the substrates as shown by various mechanical tests and very high induced stresses without peeling off. They are first described in terms of sp^2-hybridized carbon contents relatively to the sp^3-carbon ones, a parameter which influences the structure and the intrinsic diamond properties (surface roughness in the 15-35 nm range, micro-hardness, Young's modulus and residual stresses). The whole is correlated to the plasma enhanced CVD process through the formation of different concentrations of the gaseous precursors in the plasma which include both radicals and stable species as revealed by molecular beam mass spectrometry and corroborated by kinetic calculations in the C-H-O plasmas. These coatings are studied by micro-Raman spectroscopy and their structure is revealed by TEM studies. A sp^2-C enriched layer is especially evidenced at their extreme surface by Energy-Filtered TEM on transverse cross-sections, a layer which is important for tribochemical reactions. While the friction coefficient is high under ultra high vacuum, ultra low friction is obtained in saline corrosive solution. Ultra low friction with no wear is also obtained with gas phase lubrication by glycerol under boundary lubrication regime, in conditions which permit a better identification of the friction mechanism from advanced surface characterizations. These studies allow concluding that lubrication of these diamond coatings by OH-containing molecules can permit new or improved applications in various fields. Some examples of ultra low friction and low wear are provided when nano-smooth diamond coatings or alumina are sliding on nano-smooth diamond in corrosive saline solution or in the presence of glycerol lubricant, a model of environmentally friendly molecules.

11:40am **TR+SE+TF-ThM12 Tribology of Nanocrystalline Diamond Coatings**, ***N.D. Theodore***, North Carolina State University, *K.J. Wahl*, Naval Research Laboratory

The tribological behavior of several nanocrystalline diamond (NCD) coatings was compared to correlate compositional, structural, and chemical bonding differences to their friction performance. The diamond coatings were confirmed by X-ray diffraction (XRD) to be nanocrystalline with crystallite sizes ranging from to 4 to 60 nm. These diamond coatings could be differentiated from each other by their visible wavelength Raman absorption bands. Some coatings had a single strong peak at 1332 cm^{-1} typical of crystalline diamond bonding; others also had broad peaks at 1340 cm^{-1} and 1580 cm^{-1} characteristic of the D and G peaks in sp^2 hybridized carbon; and still others had additional peaks at 1135 cm^{-1} and 1470 cm^{-1}, which are commonly attributed to polyacetylene bonding. Reciprocating sliding tests using diamond counterfaces in controlled humidity environments resulted in low friction values for all coatings, between 0.02 and 0.09. The coatings exhibiting lower friction values possessed lower mean surface roughnesses, as measured using an atomic force microscope (AFM), smaller crystallite sizes, and increased amounts of non-sp^3 carbon content. Transmission Fourier transform infrared (FTIR) microscopy was used to examine the bonding chemistry in the coatings and wear tracks. The role of diamond coating microstructure, surface roughness, and bonding chemistry to the tribological behavior of NCD will be presented.

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

Tribology Poster Session

TR-ThP1 A Vacuum Tribometer to Depict Tribochemical Reactions of Lubricant Additives, ***T. Le Mogne***, *M.I. De Barros-Bouchet, J.M. Martin*, Ecole Centrale de Lyon -LTDS-, France

Today, it is well known that surface chemistry plays a key role in tribology and particularly in additives action under boundary lubrication. Tribochemical reactions are very difficult to predict because many parameters occur simultaneously in the tribological system. To simplify and to understand these phenomena, we have developed an analytical vacuum tribometer dedicated to the simulation of boundary lubrication conditions. A pin-on-flat tribometer is installed in a UHV chamber. Friction tests can be run in a wide range of surrounding partial pressures, typically from 10-8 hPa to atmospheric pressure. To study tribochemical reactions, we can introduce either pure gas or mixtures of gases (or vapours) into the chamber. Both pin and flat counterparts are introduced by a Fast Entry Load-Locks (FEL). The temperature of the flat specimen can be varied from room temperature up to 600°C. Before or after friction experiments, the two samples can be transferred without air exposure by using transfer mechanisms from the tribometry chamber into a preparation chamber and then to the analytical chamber. . This chamber is equipped with a hemispherical spectrometer build by ThermoFisher (220i). X-Ray Photoelectron Spectroscopy (XPS) can be done by using a focused monochromatic X-Ray source. A Field emission electron gun (FEG100) with a spot size lower than 1 µm allows Auger Electron Spectroscopy (AES). Ion gun (EXO5) is used for etching surfaces or for performing depth profiles. Imaging facilities are available by using a video camera for optical image, or a secondary electron detector coupled with the scanned FEG for Secondary Electron Microscopy (SEM). Chemical images can be obtained by Scanning Auger Microscopy (SAM) and XPS images by using dedicated lenses. The chemical reactivity of complex additive molecules with solid surfaces is simulated here by using small molecules with the same chemical function but with a lower molecular weight. Friction experiments are performed under variable partial pressures and at different temperatures. Mixtures of gases can be introduced to study synergistic or antagonist effects between chemical functions of additives. A residual gas analyser is installed on the vacuum chamber in order to control the purity of the gases and also to study any friction-induced outgases. We will present representative results with analyses performed inside and outside wear tracks to show chemical changes induced by tribochemical reactions.

TR-ThP2 ToF-SIMS Investigations of Tribological Layers, ***C. Bruening***, *D. Lipinsky,* University of Muenster, Germany*, S. Neudörfer, G. Poll,* University of Hannover, Germany*, H.F. Arlinghaus*, University of Muenster, Germany

The formation of tribofilms plays a critical role in the longevity of automotive gears. A wide variety of anti-wear and extreme-pressure additives are commercially available for oil modification to build tribological layers and to reduce the friction between different friction partners and enhance the stability of the gear unit. Nevertheless, the behaviour of these layers under different stresses is not well understood. For this study, friction experiments under conditions typical for gear synchronisation were performed. Under standardized conditions on a test bench, rotating synchronisation rings fitted with typical friction linings consisting of brass, scatter sinter or carbon were decelerated on stainless steel cones. As lubricant, commercial gear oil was used, containing zinc dialkyldithiophosphate (ZDDP) and calcium sulfonate acting as AW/EP additive or as detergent, respectively. ToF-SIMS with its high surface sensitivity is well suited for these investigations. It was used to characterize the tribofilms generated by the wear process. Differences in contact pressures, relative velocities of the friction partners, and durations of stress led to the generation of different tribofilms, which is indicated by TOF-SIMS spectra, lateral distribution images, and depth profiles.

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Lince, J.R.: TR+SE+TF-ThM9, **7**
Lipinsky, D.: TR-ThP2, 8
Liu, D.-L.: TR+MN+NC-WeM11, 2; TR+NS+EM+NC-WeA9, 4
Liu, J.: IS+NS+TR+NC-ThM10, 6
Loginova, E.: IS+NS+TR+NC-ThM1, 5

— M —

Martin, J.: TR+MN+NC-WeM11, 2
Martin, J.M.: TR-ThP1, 8
Maruyama, B.: IS+NS+TR+NC-ThM5, 5
Matta, C.: TR+SE+TF-ThM11, 7
McCarty, K.F.: IS+NS+TR+NC-ThM1, **5**
McGruer, N.: TR+MN+NC-WeM1, 1
Mikulski, P.T.: TR+NS+EM+NC-WeA8, 3
Miller, B.P.: TR+MN+NC-WeM5, 1; TR+MN+NC-WeM9, **2**

— N —

Naik, R.: TR+MN+NC-WeM2, 1
Neudörfer, S.: TR-ThP2, 8
Nie, X.: TR+NS+EM+NC-WeA12, 4
Nikiforov, M.P.: TR+NS+EM+NC-WeA5, 3
Nowicki, M.: TR+SE+TF-ThM1, 6

— O —

Oila, A.: TR+SE+TF-ThM5, 7

— P —

Passian, A.: TR+MN+NC-WeM10, 2
Patton, S.T.: TR+MN+NC-WeM2, 1
Perry, S.S.: TR+NS+EM+NC-WeA4, 3
Phillpot, S.R.: TR+NS+EM+NC-WeA4, 3
Pint, C.: IS+NS+TR+NC-ThM5, 5
Polcar, T.: TR+SE+TF-ThM3, 6
Poll, G.: TR-ThP2, 8

— R —

RangaPrasad, D.: TR+MN+NC-WeM10, 2
Rutledge, J.: TR+MN+NC-WeM5, 1

— S —

Salmon, N.: IS+NS+TR+NC-ThM10, 6
Sawyer, W.G.: TR+NS+EM+NC-WeA4, 3
Schall, J.D.: TR+NS+EM+NC-WeA8, 3
Schirmeisen, A.: TR+NS+EM+NC-WeA3, 3
Sharma, R.: IS+NS+TR+NC-ThM3, **5**
Sinnott, S.B.: TR+NS+EM+NC-WeA4, **3**
Slocik, J.: TR+MN+NC-WeM2, 1
So, E.: TR+NS+EM+NC-WeA11, 4
Stach, E.A.: IS+NS+TR+NC-ThM5, **5**
Stevens, K.: TR+NS+EM+NC-WeA9, 4
Stoilov, V.: TR+NS+EM+NC-WeA12, 4
Su, J.F.: TR+NS+EM+NC-WeA12, **4**

— T —

Theodore, N.D.: TR+SE+TF-ThM12, **7**
Thevuthasan, S.: IS+NS+TR+NC-ThM10, 6
Thundat, T.G.: TR+MN+NC-WeM10, 2

— V —

Vacher, B.: TR+SE+TF-ThM11, 7
Vandenbulcke, L.: TR+SE+TF-ThM11, 7
Vaughn, J.M.: IS+NS+TR+NC-ThM2, **5**
Vlastakis, B.: TR+MN+NC-WeM5, 1
Voevodin, A.A.: TR+MN+NC-WeM2, 1

— W —

Wahl, K.J.: TR+NS+EM+NC-WeA11, **4**; TR+SE+TF-ThM12, 7
Walker, M.: TR+MN+NC-WeM1, **1**
Wang, C.M.: IS+NS+TR+NC-ThM10, **6**

— Y —

Yang, J.C.: IS+NS+TR+NC-ThM11, **6**
Yang, Z.G.: IS+NS+TR+NC-ThM10, 6

— Z —

Zakharov, D.N.: IS+NS+TR+NC-ThM5, 5
Zhao, B.: TR+SE+TF-ThM2, **6**