

Monday Afternoon, November 10, 2014

Energy Frontiers Focus Topic

Room: 315 - Session EN+EM+MN+NS+TR-MoA

Energy Harvesting with Nanostructures

Moderator: Phillip Christopher, University of California - Riverside

2:00pm **EN+EM+MN+NS+TR-MoA1 Optical Engineering for Colloidal Quantum Dot Photovoltaics, Susanna Thon,** Johns Hopkins University **INVITED**

The next generation of photovoltaics seeks to improve both efficiency and cost through the use of flexible platforms and new materials. Colloidal quantum dots (CQDs), semiconductor nanoparticles synthesized from solution, are a particularly attractive material for solar energy. The bandgap of films composed of arrays of CQDs can be tuned via the quantum confinement effect for tailored spectral utilization. The performance of CQD solar cells is currently limited by an absorption-extraction compromise, whereby photon absorption lengths in the near infrared regime exceed minority carrier diffusion lengths. I will review several photonic and optical engineering schemes aimed at overcoming this compromise. These include nanophotonic and geometric light trapping techniques, as well as jointly-tuned plasmonic-excitonic photovoltaics. Additionally, I will discuss how nanoscale engineering of CQDs and related materials can lead to emergent optical properties for building color-tuned optoelectronic films.

2:40pm **EN+EM+MN+NS+TR-MoA3 Energy Transfer from Nanocrystal Quantum Dots to Si Nanomembranes Monitored via Wavelength Dependent Photocurrent Response, Weina Peng, S. Sampat, S. Rupich, B. Anand, H. Nguyen, D. Taylor, Y. Gartstein, Y.J. Chabal, A. Malko,** University of Texas at Dallas

We report the observation of wavelength dependent photocurrent in thin silicon nanomembranes (75 nm) coupled to colloidal CdSe/ZnS nanocrystal quantum dots (NQDs). The measurement was performed on back-gated, FET-type thin Si structures, which are functionalized with self-assembled monolayer (SAM) of ester termination groups to prevent surface oxidation and the formation of surface defect states. A thin film of nanocrystals is drop casted on the surface and an increase of photocurrent, up to several hundred nA, are recorded as a function of excitation wavelength on NQD/SAM/Si devices vs. plain SAM/Si structures. Quantitative analysis of photocurrent vs. NQD absorption spectrum allows us to ascribe the observed photocurrents to the photoexcited NQD excitons transferred to the underlying Si substrate via non-radiative and radiative energy-transfer mechanisms¹.

¹H. M. Nguyen, O. Seitz, W. N. Peng, Y. N. Gartstein, Y. J. Chabal, and A. V. Malko, *ACS Nano* **6**, 5574 (2012).

3:40pm **EN+EM+MN+NS+TR-MoA6 Triboelectric Nanogenerator - A New Energy Technology, ZhongLin Wang,** Georgia Institute of Technology **INVITED**

Triboelectrification is an effect that is known to each and every one probably ever since the ancient Greek time, but it is usually taken as a negative effect and is avoided in many technologies. We have recently invented a triboelectric nanogenerator (TENG) that is used to convert mechanical energy into electricity by a conjunction of triboelectrification and electrostatic induction. As for this power generation unit, in the inner circuit, a potential is created by the triboelectric effect due to the charge transfer between two thin organic/inorganic films that exhibit opposite tribo-polarity; in the outer circuit, electrons are driven to flow between two electrodes attached on the back sides of the films in order to balance the potential. Ever since the first report of the TENG in January 2012, the output power density of TENG has been improved for five orders of magnitude within 12 months. The area power density reaches 500 W/m², volume density reaches 490 kW/m³, and a conversion efficiency of ~50% has been demonstrated. The TENG can be applied to harvest all kind mechanical energy that is available but wasted in our daily life, such as human motion, walking, vibration, mechanical triggering, rotating tire, wind, flowing water and more. Alternatively, TENG can also be used as a self-powered sensor for actively detecting the static and dynamic processes arising from mechanical agitation using the voltage and current output signals of the TENG, respectively, with potential applications for touch pad and smart skin technologies. The TENG is possible not only for self-powered portable electronics, but also as a new energy technology with a potential of contributing to the world energy in the near future.

[1] Z.L. Wang "Triboelectric Nanogenerators as New Energy Technology for Self-Powered Systems and as Active Mechanical and Chemical Sensors", *ACS Nano* **7** (2013) 9533-9557.

[2] G. Zhu, J. Chen, T. Zhang, Q. Jing, Z. L. Wang* "Radial-arrayed rotary electrification for high-performance triboelectric generator", *Nature Communication*, **5** (2014) 3456.

4:20pm **EN+EM+MN+NS+TR-MoA8 Conflicting Roles of Charge Traps in ETA Solar Cells: The CREM Point of View, Hagai Cohen,** Weizmann Institute of Science, Israel

The characterization of multi-interfacial devices commonly encounters critical difficulties due to the limited access of standard electrical probes to selected inner domains. In this respect, the XPS (x-ray photoelectron spectroscopy) based CREM (chemically resolved electrical measurements) [1] is a technique proposing particularly useful capabilities. Demonstration of internal junction fields evaluation has already been provided, as well as the direct measurement of layer-specific photovoltages in ETA (extremely thin absorber) solar cells.[2] However, the complex dynamics realized during charge separation in such cells has not yet been investigated thoroughly by CREM.

The present work focuses on this issue, showing conflicting roles of charge trap states and, specifically, their different expression under controllably varied conditions. Comparison with complementary characterization techniques is further discussed, demonstrating the unique insight provided by CREM for their interpretation.

References

1. H. Cohen, *Appl. Phys. Lett.* **85**, 1271 (2004).

2. Y. Itzhaik, G. Hodes, H. Cohen, *J. Phys. Chem. Lett.* **2**, 2872 (2011).

4:40pm **EN+EM+MN+NS+TR-MoA9 Understanding Morphological and Structural Effect on Organic Photovoltaic Devices from Plasmonic Particles using Advanced Characterization Techniques, Nuradhika Herath, V. Lauter, J. Browning,** Oak Ridge National Laboratory

Organic electronics have been under intense scientific interest in recent years because of their attractive properties such as low cost fabrication processes, ability to perform under low light, and flexibility. Major achievements are based on use of new conjugated polymer and small molecules in bulk heterojunction (BHJ) devices to increase the inner donor acceptor interfaces of fully functional devices such as organic photovoltaics (OPVs) and organic light emitting devices (OLEDs). Many strategies have been introduced to enhance the power conversion efficiency (PCE) of organic electronics. Among them, one of the most promising solutions to enhance the absorption and device efficiencies of OPVs is incorporation of various metal nanoparticles (NPs). Metallic NPs enhanced the efficiency of the devices through local surface plasmonic responses (LSPR). This phenomenon reduced the recombination level of geminate excitons and increases the exciton dissociations, which enhanced the photocurrent and fill factors of devices. However, metallic NPs blended within the active layer can act as polaron traps detracting the device performances. In this study, we investigate layer and interfacial structure of small molecule (SM), *p*-DTS(FBTTh₂)₂ and fullerene, PC₇₀BM system incorporated with silver (Ag) NPs, using neutron reflectometry (NR), X-ray reflectometry and Atomic Force Microscopy (AFM). We present detailed composition changes with Ag NPs concentrations along the film depth to understand morphological and dynamical effects of BHJ devices incorporated with plasmonic particles. To complement and enhance the findings from NR, we report optical properties of the samples using UV-Visible absorption and Photoluminescence spectroscopy. Our findings provide unique information and clear insights into dynamics of plasmonic organic solar cells and their future applications for further enhancement of PCE.

This research was conducted at Spallation Neutron Source and at the Center for Nanophase Materials Sciences, which is sponsored at ORNL by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Department of Energy.

5:00pm **EN+EM+MN+NS+TR-MoA10 Doped TiO₂ Based Core-Shell Structures for High Efficiency Hybrid Solar Cells, Jonas Weickert, J. Dorman, M. Noebels, M. Putnik, T. Pfadler,** University of Konstanz, Germany, A. Wisnet, C. Scheu, LMU Munich, Germany, L. Schmidt-Mende, University of Konstanz, Germany

Hybrid solar cells, with an inorganic/organic interface for charge separation, have been extensively investigated in the past decade in order to replace the expensive Si based technology with an inexpensive alternative. Typically, these devices incorporate a mesoporous TiO₂ film which is decorated with dye molecules and filled with a hole transport polymer, for example P3HT,

to conduct the electrons and holes, respectively. Recently, we have shown that the efficiency of nanowire based hybrid solar cells can be increased from ~1.8 % to 2.5 % through the formation of a Sn-doped TiO₂/TiO₂ core-shell device created via a hydrothermal growth and subsequent TiCl₄ treatment. However, this surface treatment presents difficulties in creating a crystalline conformal coating, limiting the control over the extent of coating and the crystallinity, directly affecting the charge injection from the polymer into the TiO₂ array. In this work, we directly deposit a controllable TiO₂ film through atomic layer deposition to conformally coat the nanowire arrays with various thicknesses. By changing the thickness and TiO₂ crystallinity, we are able to engineer the energy levels at the TiO₂-dye-P3HT interface due to the magnitude and position of the Fermi levels of the core and shell material, influencing the rate of charge injection and recombination. Furthermore, the crystallinity of the shell layer directly affects the amount of dye that can be absorbed on the surface of the nanostructures with a reduction in light absorption by roughly 30% from anatase to rutile TiO₂. Finally, a detailed mechanism will be proposed for the device performances based on the energy level alignment between the pinned Fermi-level TiO₂ structure and the HOMO of the P3HT resulting in a shifting open circuit voltage based on the crystal phases. Additionally, the core-shell structures are characterized with photovoltage decay and impedance spectroscopy measurements to study the charge transport and recombination across these various interfaces.

5:20pm **EN+EM+MN+NS+TR-MoA11 Stack Numbers Dependence of the Activation Energies for Carrier Escape from and Recombination in Strain-Balanced InGaAs/GaAsP MQW**, *Atsuhiko Fukuyama, T. Ikari, K. Nishioka, T. Aihara, H. Suzuki*, University of Miyazaki, Japan, *H. Fujii, M. Sugiyama, Y. Nakano*, The University of Tokyo, Japan

Fabrication of multiple quantum well (MQWs) in an absorption layer can extend the absorption region toward a longer wavelength and enhance the short-circuit current in the solar cells. However, MQWs function as recombination centers, leading to degradation in both open-circuit voltage and fill factor. We have already reported that the increase in stack number of QW causes the degradation of carrier collection efficiency [1]. In this study, we investigate the effects of stacks number on temperature dependences of the photoluminescence (PL), photothermal (PPT) and the surface photovoltage (SPV) signals. Although the photoexcited carriers in the barrier should relax by the radiative recombination (PL), carriers can thermally escape (SPV) or non-radiatively recombine (PPT) at the same time. Therefore, the latter two methodologies give us new insights for the carrier recombination and drift through the QW.

The present strain-balanced InGaAs/GaAsP MQWs absorption layer was composed of a 7.0-nm-thick In_{0.25}Ga_{0.75}As well and a 10.8-nm-thick GaAs_{0.66}P_{0.34} barrier. All layers were grown on an *n*-type GaAs substrate using metal-organic vapor phase epitaxy. We prepared different samples with MQW stack numbers of 10, 20, 30, and 40 in the *i*-region.

All PPT and SPV spectra showed three distinctive peaks followed by a step like function. They were decomposed into inter-subband transitions expressed by the two dimensional density of states for the QW and exciton peaks [2]. Although the PL intensity decreases with increasing the temperature, signals for PPT and SPV increases. We suppose two activation energies for the process: one is that for the carrier escape from the QW and another is for the non-radiative recombination in the QW. The three rate equations were built for PL, PPT and SPV and the temperature dependences are numerically fitted to estimate the two activation energies. As a result, we have estimated the activation energy for carrier escaping from the QW is constant as 70 meV for all samples with different stacks number. This is the same as the calculated barrier height. However, the activation energy for the non-radiative recombination increases from 6 to 49 meV for the sample with 10 and 40 stacks. This means that radiative recombination increases with increasing the stack number. The carriers thermally escape from the QW again relax into next well and may contribute to increase the radiative recombination.

[1] H. Fujii et al., Jpn. J. Appl. Phys. **51**, 10ND04 (2012).

[2] M. Kondow, A. Fukuyama, and T. Ikari et al., Appl. Phys. Express **2**, 041003 (2009).

Advanced Surface Engineering Room: 302 - Session SE+NS+TR-TuM

Nanostructured Thin Films and Coatings

Moderator: Robert Franz, Montanuniversität Leoben,
Andrey Voevodin, Air Force Research Laboratory

8:00am **SE+NS+TR-TuM1 Electrostatic Coating with Ligandless Copper Nanoparticles**, *Lance Hubbard, A.J. Muscat*, University of Arizona

Physical vapor deposition is currently used to deposit copper seed layers in through Si vias, but this approach is already close to its limit and may not be an option for future scaling of high performance integrated circuits. An alternative is electroless deposition (ELD) since it produces conformal, selective coatings at low temperature. ELD occurs by chemical reduction of metal ions without an externally applied potential. In the conventional approach, a metal catalyst such as Pt, Pd, or Ni is used that can be both expensive and increase the resistance of interconnect lines. Previous work was done in an aqueous phase using a complexing agent or polymer to protect the particles. Good film continuity was demonstrated, but the sheet resistance was low.^{1,2} In this study, we report on a nonaqueous ELD process that uses a charge compensator, but not a ligand or complexing agent. The weak electrostatic attachment of the charge compensator to the ions and particles in solution and the high pH conditions improve the driving force for metal deposition. Si(100) coupons were hydroxylated using sulfuric acid-hydrogen peroxide mixture. The surface was terminated with an amine adhesion layer by immersion in a 4 mM solution of either (3-aminopropyl)-trimethoxysilane (APTMS) or (3-mercaptopropyl)-trimethoxysilane (MPTMS) in methanol followed by a 150°C anneal. Metal films were deposited by suspending samples in a bath made by dissolving Cu(II) chloride in ethylene glycol, which also served as the reducing agent, and adding 1-butyl-3-methylimidazolium tetrafluoroborate as a charge compensator. The surface plasmon resonance (SPR) peak of the Cu nanoparticles in the bath and film was at 585 nm. Light scattering measurements and transmission electron microscopy (TEM) images yielded a size distribution of 3.1±1.6 nm. The complex consisting of the Cu particle core and ion shell is attracted to the positively charged amine groups at high pH, and a thin metal film is deposited that is both continuous and cohesive. Annealing the coupons at 200°C in nitrogen promoted the formation of an electrically conductive film. Electron microscopy images of the coated substrates show a 20-50 nm thick film of 3 nm dia. particles; spectroscopic ellipsometry shows both bulk and nanophase properties. Four-point probe measurements of the films yielded electrical conductivities in the range 10⁵-10⁶ S/m (bulk Cu conductivity 4-6×10⁷ S/m).

References

- 1) Armini and Caro, J. Electrochem. Soc. 2010, 157(1), D74-D80, doi: 10.1149/1.3258026.
- 2) Inoue et al. J. Electrochem. Soc. 2012, 159(7), D437-D441, doi: 10.1149/2.070207jes.

8:20am **SE+NS+TR-TuM2 Electrically Stable Pt-ZrB₂ Nanocomposite Thin Films for High Temperature Applications**, *Julia Sell, D.M. Stewart, G.P. Bernhardt, D.J. Frankel, R.J. Lad*, University of Maine

Considerable cost savings could be achieved by incorporating high temperature sensors into high temperature machinery to optimize processes and monitor materials degradation. However, in order to achieve reliable sensor operation, the thin film electrodes, sensing elements, and packaging materials must remain stable over long times at high temperature. Metallic thin films, such as Pt, agglomerate and lose conductive pathways quickly when exposed to temperatures exceeding 700°C. In this work, we show that Pt-ZrB₂ nanocomposite films retain a continuous morphology and remain electrically conductive up to at least 1100°C in air. Nanolaminate Pt-ZrB₂ films comprised of ten alternating layers of Pt and ZrB₂ were deposited to a total thickness of 200nm at ambient temperature onto sapphire substrates using e-beam evaporation. Annealing the nanolaminate films above 800°C in air causes intermixing, resulting in a nanocomposite Pt-ZrB₂ film architecture. Film electrical conductivities were measured using a 4-point probe as a function of time and temperature in air up to 1200°C. These results show that Pt-ZrB₂ nanocomposite films have conductivities in the 10⁶-10⁷ S/m range and remain stable above 1000°C, but that the overall conductivity and stability depends on the Pt-ZrB₂ layer thickness ratio. Analysis via x-ray photoelectron spectroscopy and x-ray diffraction indicates that both monoclinic and tetragonal ZrO₂ nanocrystallites are formed in the films during the annealing treatment, and they serve to hinder

agglomeration of the Pt phase. Scanning electron microscopy shows highly conductive Pt-rich pathways in the films that coexist with the ZrO₂ phase. Some films were coated with an amorphous Al₂O₃ protective capping layer using atomic layer deposition (ALD), and this capping layer helped to limit oxygen diffusion into the films, thereby increasing the long term stability of film conductivity.

8:40am **SE+NS+TR-TuM3 A Novel Reactive Plasma-Assisted Coating Technique (RePAC) for Thin BN/Crystalline-Si Structures and their Mechanical and Electrical Properties**, *Koji Eriguchi*, Kyoto University, Japan, *M. Noma*, SHINKO SEIKI CO., LTD., Japan, *S. Hasegawa*, Osaka University, Japan, *M. Yamashita*, Hyogo Prefectural Institute of Tech., Japan, *K. Ono*, Kyoto University, Japan

Cubic boron nitride (c-BN) has attracted much attention as a hard coating film on cutting tools, owing to its high oxidation resistance and hardness—the second hardest material to diamond. Although various methods of forming c-BN films on various substrates have been proposed, the interface between c-BN and the substrate material was unstable against delamination and oxidation [1] after long-time machining and air exposure. In this study, we propose a novel reactive plasma-assisted coating technique (RePAC) for forming sub-μm-thick BN film directly on crystalline Si substrates, where magnetically-confined high-density Ar/N₂ plasma was generated with a stable anodic current to promote the reaction between N radicals and B atoms evaporated onto a Si substrate placed on a sample stage [2]. Controlling substrate bias voltage V_{sub} in the RePAC, we fabricated various thin-BN/Si structures and identified a correlation among the properties such as mechanical hardness, friction coefficient, leakage current, and dielectric constants. TEM analyses revealed that nano-structures of the BN films were varied from bulk amorphous (a)-BN, layered hexagonal (h)-BN, to c-BN phase in turbostratic (t)-BN domain, in accordance with V_{sub} ($|V_{\text{sub}}|=10-120$ V). We speculate that bombardment of incident ions (Ar⁺ and/or N₂⁺) plays a key role in forming these characteristic features, in addition to stoichiometric N and B contents. Moreover, we clarified the high hardness (> 4000HK, by the Knoop indenter) and the dielectric constant higher than previously-reported values (10–20, by the electrical capacitance measurement) for the present thin c-BN/Si structure with anti-delamination feature after long-time air exposure. The obtained results suggest that the present BN film formed by the RePAC has wide applications not only as a hard coating film but also as a high dielectric-constant layer in electronic devices.

[1] For example, P. B. Mirkarimi *et al.*, Mater. Sci. Engin., **R21**, 47 (1997).

[2] M. Noma *et al.*, Jpn. J. Appl. Phys. **53**, 03DB02 (2014).

9:20am **SE+NS+TR-TuM5 Multifunctional Protective Coatings for Aerospace Applications**, *Etienne Bousser, L. Martinu, J. Klemberg-Sapieha*, Ecole Polytechnique de Montreal, Canada **INVITED**

Ever increasing technical, economic and environmental requirements give rise to situations where modern equipment and components are often pushed beyond the limits of their design capabilities. This frequently leads to tribological deficiencies, such as lubrication breakdown, excessive wear and tribo-corrosion, resulting in increased operational costs, decreased efficiency and premature failure. Therefore, appropriate material's selection for a given application must be guided by an accurate understanding of the intervening tribological processes while ensuring the maintained functionality of the surface for optimal application performance.

Solid Particle Erosion (SPE) occurs in situations where hard particles, present in the environment, are entrained in a fluid stream, and impact component surfaces such as in aircraft engines. It is well known that ductile materials erode predominantly by plastic cutting or ploughing of the surface, while brittle materials do so by dissipating the particle kinetic energy through crack nucleation and propagation. In the first part of this presentation, we examine the mechanisms by which surfaces dissipate the kinetic energy of impacting particles, and discuss the erosive response of hard protective coating systems. We investigate the means by which surface engineering can enhance erosion resistance, and correlate surface mechanical properties to the erosion behaviour. In addition, we will show that the architectural design of advanced coating systems is also well supported by finite element modelling of single particle impacts of the coated surfaces.

The second part of the talk will focus on the reparability of advanced coating systems. Indeed, because of the high fabrication costs of engine components, it is desirable to develop an effective and efficient industrially-viable technique to remove defective coatings with the aim of recycling the costly engine components. In particular, we will present our recent studies on the removal of TiN-based erosion resistant coatings using a non-line-of-

sight reactive ion etching technique and a complementary laser ablation process.

11:00am **SE+NS+TR-TuM10 Hard Coatings with Designed Thermal Conductivity**, *P.H.M. Boettger*, Empa, ETH Zurich, Switzerland, *V. Shklover*, ETH Zurich, Switzerland, *M. Sobiech*, Oerlikon Balzers Coating AG, Liechtenstein, **Joerg Patscheider**, Empa, Switzerland

Hardness, thermal stability and oxidation resistance are often the main properties to optimize for most tool coatings developments for industrial applications. The thermal conductivity, however, has been regarded to a much lesser extent as property to improve tool life. So far, only little attention has been given to this fact and the explicit role of thermal conductivity in machining Ti and Ni-based alloys. These materials typically have low thermal conductivity, as well as modern tool coatings such as CrAlN and TiAlSiN. This unfavorable combination may lead to the formation of thermal hot spots during machining, which adds to the premature degradation of such coatings. For these reasons the thermal conductivity is an important process parameter.

This talk will discuss the relations between hardness, coatings architecture and thermal conductivity and how advanced coatings can be tuned to achieve significant anisotropy of the thermal conductivity. In arc-evaporated $\text{TiO}_x\text{N}_{1-x}$ and $\text{CrO}_x\text{N}_{1-x}$ thermal conductivity can be adjusted in a wide range between 2 and 35 W/m·K, while keeping hardness and oxidation resistance intact. The data for single phase oxynitrides as well as of multilayered coatings agree well with a newly developed model based on constant phonon scattering cross section of the introduced oxygen. It will be shown how temperature-mitigating multilayer coatings can be prepared using these materials by introducing highly anisotropic thermal conductivity.

11:20am **SE+NS+TR-TuM11 Microstructure and Hardness Gradients in Sputtered CrN Films**, *A. Riedl*, Materials Center Leoben, Austria, *R. Daniel*, Montanuniversität Leoben, Austria, *T. Schoeberl*, *M. Stefenelli*, Austrian Academy of Sciences, *B. Sartory*, Materials Center Leoben, Austria, *J. Keckes*, **Christian Mitterer**, Montanuniversität Leoben, Austria

Hardness and elastic modulus of a sputtered nanocrystalline CrN thin film, grown under varying ion bombardment conditions, were studied by nanoindentation using a depth-profiling technique and related to cross-sectional X-ray nanodiffraction data on the local microstructure. Changes in texture are shown to have almost no effect on the elastic modulus due to the isotropic response of the polycrystals. However, the locally varying growth conditions, which affect crystal size and number, determine the hardness values across the film thickness. Regions with highly distorted small crystals result in higher hardness in comparison to those with well-developed coarsened grains. This work confirms the notion of the existence of growth-related hardness gradients in single-phase nanocrystalline thin films.

11:40am **SE+NS+TR-TuM12 Development of Low Friction Nanocomposite Coatings for Diesel Engine Piston Rings**, **Jianliang Lin**, *R. Wei*, *K. Coulter*, *C. Bitsis*, *P.M. Lee*, Southwest Research Institute

Hard and thick (15-20 μm) TiSiCN nanocomposite coatings have been developed to improve the wear resistance and reduce the overall average friction for diesel engine piston rings. The coatings were deposited by sputtering Ti metal targets in a reactive atmosphere using a plasma enhanced magnetron sputtering (PEMS) process. The reactive mixture contains argon, nitrogen, acetylene gases, and hexamethyldisilazane vapor which were introduced into the chamber using a liquid evaporation/delivery system. The substrates were AISI 304 stainless steel coupons and piston rings. The TiSiCN coatings with different elemental compositions and microstructures were prepared by varying the hexamethyldisilazane and acetylene gas/vapor concentrations and the target power. The microstructure of the coatings was characterized using scanning electron microscopy, energy dispersive spectroscopy, and X-ray diffraction. The adhesion strength and mechanical and tribological properties of the coatings were measured using HRC tests, nanoindentation and ball-on-disk wear tests. By optimizing the composition and microstructure of the coatings, thick TiSiCN nanocomposite coatings with excellent adhesion and a dry sliding friction less than 0.2 have been obtained. The optimized coating systems were applied on the piston rings, which were evaluated on a Plint TE77 reciprocating bench rig and in the real diesel engine test. The principle for the increased wear resistance and the potential applications will be discussed in the paper.

Thursday Morning, November 13, 2014

Tribology Focus Topic

Room: 303 - Session TR+NS-ThM

Bridging Scales in Tribology

Moderator: J. David Schall, Oakland University

8:00am **TR+NS-ThM1 Temporal and Spatial Multiscale Simulations of Low-Velocity Frictional Sliding, Woo-Kyun Kim**, University of Cincinnati **INVITED**

As the size of mechanical systems of technological interest such as micro electro-mechanical systems (MEMS) decreases, the need to develop experimental and theoretical tools to investigate micro/nanometer scale phenomena has been growing rapidly. Since its invention in 1986, the Atomic Force Microscope (AFM) has been a primary tool to study the atomic-scale friction and wear and atomistic simulation methods such as molecular dynamics (MD) have also been widely used because these simulations can provide direct access to atomic-scale mechanisms which cannot be observed experimentally. However, there is a great disparity in length and time scales between the simulated systems and the real experimental systems. One of the significant artifacts of these scale differences is that systems are loaded at by several orders of magnitudes larger rates in simulations than in experiments, which may completely distort the underlying mechanisms. Recently, a novel multiscale method, called hyper-QC, which can span both length and time scales simultaneously has been developed. Hyper-QC combines quasicontinuum (QC), a spatial multiscale method, and hyperdynamics, an accelerated MD scheme, in a single platform. In this talk, the hyper-QC simulation results of AFM experiments will be presented. Hyper-QC enables the reduction in the sliding rate by two or three orders of magnitudes from that of the conventional MD scheme as well as the reduced effective number of atoms that is achieved through the QC coarse-graining.

8:40am **TR+NS-ThM3 Crystal-Amorphous and Amorphous-Amorphous Transitions in Carbon under Tribological Load, Lars Pastewka**, Karlsruhe Institute of Technology, Institute for Applied Materials IAM, Germany **INVITED**

Diamond and amorphous carbon (aC) are prototypical examples of wear resistant materials. Yet, these materials wear down, but little is known about the atomic scale processes that cause wear. Molecular dynamics is ideally suited to gain a deeper understanding of the underlying wear processes [1]. Such atomic-scale simulations reveal that both, mechanical and oxidative wear actions are active. Mechanical action transforms the material to a weaker state that is then easily oxidized. For diamond, we find a transition to an aC, while we find a high-density—low-density aC-aC transition for amorphous thin films. The velocity of the diamond/aC interface depends crucially on the diamond surface orientation with the highest speed found for (110) surfaces that are rubbed in the (001) direction, while the lowest interface speed was observed for the diamond (111) surface. High-density aC itself transforms even faster to a low density state that then succumbs to wear [2]. We relate the aC-aC transition to shear-banding in plasticity of amorphous materials, and argue that the formation of shear-bands is crucial for the wear resistance of carbon based hard coating. These findings are in perfect agreement with a 600 years old experimental knowledge of diamond polishers, and with recent experiments comparing wear in diamond and amorphous carbon thin films.

[1] L. Pastewka, S. Moser, P. Gumbsch, M. Moseler, Nat. Mater. 10, 34 (2011)

[2] T. Kunze, M. Posselt, S. Gemming, G. Seifert, A.R. Konicek, R.W. Carpick, L. Pastewka, M. Moseler, Tribol. Lett. 53, 119 (2014)

9:20am **TR+NS-ThM5 A Molecular Dynamics Investigation of the Atomic-Scale Wear of Carbon-Based Materials Upon Repetitive Contact, Kathleen Ryan**, United States Naval Academy, V. Vahdat, University of Pennsylvania, P.L. Keating, United States Naval Academy, Y. Jiang, K.T. Turner, R.W. Carpick, University of Pennsylvania, J.A. Harrison, United States Naval Academy

Amplitude modulation atomic force microscopy (AM-AFM) involves hundreds of thousands of contacts between a tip and surface per second. Each contact can result in the formation and breakage of chemical bonds causing wear to the tip. Atomic-scale wear hinders the quality and reproducibility of structures created by tip-based nanomanufacturing processes. However, wear cannot be analyzed at the single-atom level using existing experimental methods. Continuum mechanics models can be used to estimate stresses, deformations, and the work of adhesion. However, these models can break down at the nanoscale as they rely upon

assumptions about the tip shape and material properties, and ignore the discrete atomic structure of the materials. Molecular dynamics (MD) simulations allow the nanoscale behavior to be modeled by resolving the positions, velocities, and forces of all atoms in the system. Here, MD simulations are used to model the repeated contact of an axisymmetric, hydrogenated amorphous carbon (a-C:H) tip with a 3-dimensional ultrananocrystalline (3D UNCD) surface. Using a finite element method to select the smallest portion of the tip that should be modeled atomistically, the tip radius could be set at 15 nm, much larger than previous simulations of this type and in the range of experimental AFM tip sizes. Tip/surface material and tip shapes were also chosen to closely mimic those used in comparable experiments. The wear processes, including adhesive forces, material transfer, and changes to material hybridization are examined following multiple contact cycles. We observe discrete atomic bonding and transfer events, as opposed to plastic deformation or fracture of multi-atom clusters. This is consistent with interpretations of experimental wear behavior and adds significant new detail to the possible pathways for the wear process.

9:40am **TR+NS-ThM6 The Buried Interface: In Situ Methods for Tribology, Brandon Krick**, Lehigh University, K.G. Rowe, A.I. Bennett, D.W. Hahn, W.G. Sawyer, University of Florida

Tribological phenomena occur at interfaces which are often difficult to directly observe or access. *In situ* techniques are rapidly emerging to probe surfaces buried at an interface, illuminating the physical, mechanical and chemical interactions between two surfaces in intimate contact. In this presentation, we discuss several *in situ* techniques, including optical microscopy of the real area of contact, thermal imaging of contact temperature, and Surface Plasmon Resonance of molecular transfer of a solid lubricant during sliding.

Utilizing an optical *in situ* microtribometer, we can explore the real area of contact and near contact surface topography of contacting surfaces; this technique has been used to visualize adhesive-elastic contact between a rigid sphere and a thin elastic foundation as well as randomly rough elastomer surface in contact with an infinitely stiff and flat (by comparison) surface. Similarly, an forward looking infrared (FLIR) microscope camera can reveal interface temperatures with microscopic resolutions. Finally, an *in situ* Surface Plasmon Resonance (SPR) tribometer is used to measure molecular-scale transfer of solid lubricants during sliding. For some systems, such as PTFE, transfer is detected as early as the first cycle of sliding, while minimal transfer is observed in other systems such as UHMWPE.

11:00am **TR+NS-ThM10 Contact and Friction Between Rough Adhesive Surfaces: From Atomic to Micrometer Scales, Mark Robbins**, Johns Hopkins University, L. Pastewka, Fraunhofer Institute for Mechanics of Materials IWM, Germany **INVITED**

Experimental surfaces typically have roughness on a wide range of length scales. This roughness greatly reduces the fraction of the area that is in intimate molecular contact and thus can contribute to friction and adhesion. The talk will first describe recent numerical calculations of elastic contact between rough surfaces with nominally flat or spherical geometries on large scales. An efficient Greens function approach allows calculations for systems with roughness on nanometer to micrometer scales to be performed with atomic resolution in the contact. Results for a wide range of geometries can be collapsed using simple scaling relations that depend on the root mean squared surface slope, sphere radius, elastic modulus, and work of adhesion. The scaling relations explain why adhesive interactions have little effect unless the surfaces are extremely smooth or soft. The traditional Fuller-Tabor model for adhesion of rough surfaces is shown to be qualitatively inconsistent with the simulations. The effect of atomic scale plasticity on contact and adhesion is surprisingly small. The talk will conclude by considering how forces in the contact area give rise to friction at larger scales.

11:40am **TR+NS-ThM12 Scaling Properties of Measured Frictional Parameters in Microscale Contacts, Brian 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 ($> 1 \text{ m/s}$) during the initiation of full slip. Energy dissipation, lateral contact stiffness, and amplitude of motion are measured for a transverse-shear quartz resonator in contact with a small spherical probe. Averaged values for the elastic and dissipative forces are derived as functions of shearing amplitude, at constant normal loads in the range from 10 μN to 8 mN. We observe a transition from partial to full slip at a threshold amplitude of motion, characterized by a maximum elastic force. Kinetic friction in the full-slip regime is observed to be about a factor of two smaller than this elastic force limit. Data from tests at

various normal loads can be collapsed onto common curves by normalizing the forces and amplitudes according to their characteristic values. We discuss the observed scaling of these frictional parameters with the size of the contact and the extent of agreement with current theories of microslip.

12:00pm **TR+NS-ThM13 Scale Effects in Single-Asperity Friction.**
Tristan Sharp, Johns Hopkins University, *L. Pastewka*, Fraunhofer Institute for Mechanics of Materials IWM, Germany, *M.O. Robbins*, Johns Hopkins University

Simulations are used to examine the static friction in model single-asperity contacts between a rigid sphere and a flat elastic substrate. The sphere radius R and the contact radius a are varied from nanometers to micrometers. First the case of commensurate contact between identical aligned surfaces with repulsive interactions is considered. For small contacts all contacting atoms move coherently and the friction coefficient μ is independent of contact radius and load. In larger contacts, interfacial slip is mediated by localized dislocations. At first μ decreases with increasing contact radius: $\mu \sim (Ra_0)^{1/2}/a$, where a_0 is the nearest-neighbor spacing. At even larger contact sizes, μ begins to drop more slowly. The results are in sharp contrast to Cattaneo-Mindlin continuum theory where μ is independent of contact size. Separate simulations are performed to connect the results to the dislocation-based models of contact-size effects due to Hurtado and Kim, and Gao, which assume adhesive interactions between surfaces and find $\mu \sim (a_0/a)^{1/2}$. The talk will conclude with discussions of the effect of changes in the relative alignment of crystalline axes.

Thursday Afternoon, November 13, 2014

Tribology Focus Topic

Room: 303 - Session TR-ThA

Tribology in Unique Environs

Moderator: Kathleen Ryan, United States Naval Academy

3:00pm **TR-ThA3 Molecular Mechanisms of Aqueous Boundary Lubrication by Mucinous Glycoproteins**, *Stefan Zauscher*, Duke University **INVITED**

In this talk I will focus on lubricin and surface zone protein, secreted, cytoprotective glycoproteins, encoded by the gene PRG4, that are essential to maintaining joint function and long-term integrity of synovial joints by providing boundary lubrication, preventing cartilage-cartilage adhesion, and mediating adsorption of cells and proteins. Specifically I will report on our results from nanotribo-mechanical measurements on model surfaces and cartilage, combined with other surface specific, physicochemical measurements that shed new light on the mechanisms by which PRG4 provides lubrication and wear protection in diarthrodial joints. Furthermore, I will report on the interaction of PRG4 with collagenous model surfaces. Taken together, our results suggest that the role of effective boundary lubricants in mediating friction in articular joints is largely one of wear protection of surface asperities, by maintaining the surfaces in a nonadhesive mode and causing shear dissipation in the biopolymeric boundary lubricant layer, even at the cost of attaining "high" coefficients of friction ($\text{COF} \sim 0.15$). Our results also contribute to the understanding of the conformation and physico-chemical function of mucinous glycoproteins on biological interfaces.

4:00pm **TR-ThA6 Unusual Friction and Wear Behavior of Graphene in Different Environments**, *Ali Erdemir, D. Berman, A.V. Sumant*, Argonne National Laboratory **INVITED**

Graphene is a remarkable 2D material made of one-atom-thick carbon layer. Its unusual electrical, thermal, optical, and mechanical properties make it a promising material for numerous industrial applications. Recently, graphene was also shown to exhibit unusual tribological properties when used at sliding contact interfaces. In our laboratory, we have been exploring friction and wear behavior of graphene using nano-to-macro-scale tribological test systems and out of our research, we have discovered that a few layers of graphene on sliding surfaces can last tens of thousands of sliding cycles and the rubbing surfaces where graphene is applied to suffer very little or in some instances no wear. Friction was also dramatically reduced. We have found that graphene works equally well in humid or dry test environments; thus contrasting the very high environmental sensitivity of other solid lubricants like graphite or molybdenum disulfide. Our more recent studies have confirmed that even one layer of graphene put on a steel surface has a lifetime of more than 6000 cycles in hydrogen and the rubbing surfaces show no sign of wear. When 2 to 3 layers of large graphene sheets were applied, the lifetime increases to more than 30,000 cycles. Furthermore, under the right test conditions or against the right kind of counterfaces, graphene has the ability to literally vanish friction. This and other tribological observations point to a unique lubrication mechanism for graphene. In this talk, we will provide a comprehensive overview of recent experimental findings regarding the unusual friction and wear behavior of graphene and try to explain why it is so effective in drastically reducing friction and wear despite being only one atom thick.

4:40pm **TR-ThA8 Tribological Properties and Effects of Water on Carbon-Based Materials using Molecular Dynamics Simulations**, *Marcel Fallet, K.E. Ryan*, United States Naval Academy, *M. Knippenberg*, High Point University, *P. Mikulski, J.A. Harrison*, United States Naval Academy

Tribological studies of C-based materials have come to the forefront of experimental and computational chemistry with applications for microfluidic devices and tip-based nano-manufacturing. The effects of humidity on friction and adhesion of some carbonaceous materials underscore the need to understand underlying mechanisms. Since it is difficult to determine atomic-scale behavior via experimental methods, molecular dynamics simulations have been employed to examine this behavior. Sliding simulations of non-hydrogenated, ultrananocrystalline diamond (UNCD) surfaces in the presence of water using the qAIREBO potential¹ have been performed. This reactive, bond-centric potential can model charge in C, H, and O systems. Hybridization changes, cross-sectional distributions of water, charge distributions, and other results will be presented to better understand the tribological impact of water in these systems.

5:00pm **TR-ThA9 An Atomistic Investigation of Tribological Performance of Solvated Nanodiamonds**, *Farshad Saberi-Movahed, D. Brenner*, North Carolina State University, *O.A. Shenderova*, International Technology Center

Nanodiamonds synthesized by detonation of explosives have emerged as a promising additive to base lubricants to reduce wear and friction. Several mechanisms have been suggested for this observation, including creation of protective surface films, surface roughness reduction by abrasion and by filling in surface regions between asperities and by acting as spacers that roll and slide between contacting surfaces.

To better understand the details of these various mechanisms, and how these details relate to nanodiamond and surface structure and properties, we have been carrying out molecular dynamics of solvated nanodiamonds between sliding interfaces. Our initial simulations have focused on understanding the role of particle shape (round versus faceted) on viscosity of base fluid, the motion of the nanodiamond (sliding versus rolling), and correlation time of the nanodiamond motion as a function of pressure, and the interface sliding speed and separation. For example, we have observed that at higher nanodiamond volumetric ratio, the viscosity of water increased. It was also observed that the viscosity of the nanofluid decreased as the temperature increased. Simulation results for nanodiamonds with different surface functional groups, agglomerated nanodiamonds and nanodiamonds reacting with metal surfaces during sliding will be discussed, as well as studies using non-aqueous solvents.

This material is based upon work supported by the G8 Research Council through the National Science Foundation under Grant No. CMMI-1229889

5:20pm **TR-ThA10 Quantitative Analysis by AES and XRD and Tribological Properties of Multilayers and Nanocomposites Based on Titanium Nitride**, *Arturo Talledo*, Universidad Nacional de Ingeniería, Peru, *J.A. Huaranga, J.L. Ampuero, J.J. Asmat, K. Paucar, C. Benndorf*, Universidad Nacional de Ingeniería, Perú

Multilayers and nanocomposites based on titanium nitride are widely investigated due to their high hardness and tribological properties. In this paper we report the production of coatings, on high speed steel, made by dc magnetron sputtering of multilayers TiN/VN, TiN/CrN and TiN/SiN as well as nanocomposites consistent in nanoparticles of SiN or CrN or VN embedded in matrixes of TiN. All these coatings were investigated by Auger Electron Spectroscopy and X-ray diffraction. Stoichiometry and structure were related to their respective Vickers hardness (measured by using Scanning Electron Microscopy), friction coefficient and abrasion wear measurements.

Thursday Evening Poster Sessions

Tribology Focus Topic

Room: Hall D - Session TR-ThP

Tribology Poster Session

TR-ThP2 Nanocomposite Hf-B-C Hard Coatings by Low Temperature CVD, Elham Mohimi, J.R. Abelson, T. Ozkan, K. Walsh, S. Babar, P.J. Semprrott, G.S. Girolami, University of Illinois at Urbana Champaign, A.A. Polycarpou, Texas A&M University

Nanocomposite coating materials can afford an excellent combination of chemical, physical and mechanical properties, including high or super-hardness along with toughness. There is an extensive literature concerning the growth and properties of transition metal nitride, carbide and boride materials, as well as ternary (pseudo-binary) combinations. Our group previously reported the conformal growth and favorable mechanical properties of HfB₂ and Hf-B-N hard coatings by chemical vapor deposition (CVD) using the high vapor pressure precursor hafnium borohydride, Hf(BH₄)₄, at substrate temperatures below 300°C. Our objective is to extend the use of the HfB₂ system for tribological applications, for which a low coefficient of sliding friction is desirable. A useful analogue is C-alloyed TiB₂, which exhibits super-hardness and good thermal stability. However, there have been no previous reports of the growth and properties of Hf-B-C alloys.

We report the CVD of Hf-B-C nanocomposite coatings on Si and on steel discs using hafnium borohydride precursor with a co-flow of dimethylbutene (DMB), (CH₃)₃CCH=CH₂, as the carbon source. Depositions are performed in a high vacuum chamber with 0.1-0.5 mTorr of hafnium borohydride and 0.1-0.4 mTorr of DMB at a substrate temperature of 250-700 °C. The resulting carbon contents are 10-33 at. %. DMB acts as growth inhibitor which reduces the film growth rate by a factor of 2-6 compared to growth using the precursor alone; for high temperature depositions, DMB also enhances the film density and decreases the surface roughness. XPS analysis indicates that Hf-B-C films consist of a mixture of HfB₂, HfC and B₄C phases. As-deposited films are XRD amorphous with hardness values of 8-10 GPa and reduced modulus of 92-120 GPa. Upon annealing at 700°C for 3 hrs, the films transform partially to a nanocrystalline structure, which increases the hardness and modulus. Multilayer films of (HfB₂ / Hf-B-C)_n afford a means to engineer the hardness and modulus to desirable values. The tribological properties of Hf-B-C films are superior to those of HfB₂ films. This system affords conformal coating at low growth temperature, suitable for complex structures such as MEMS.

TR-ThP3 Stress Analysis of TiSiN and TiAlN Coatings using Scratch Testing and Raman Spectroscopy, Johans Restrepo, Instituto de Investigaciones en Materiales - UNAM, Mexico, E. Camps, Instituto Nacional de Investigaciones Nucleares, Mexico, S. Muhl, Universidad Nacional Autónoma de México

The TiSiN and TiAlN coatings were deposited using Pulsed Laser Deposition. The films were characterized by SEM-EDS (chemical composition and surface morphology), X-ray diffraction (crystalline structure and grain size) and Nanoindentation (hardness and Young's modulus). The tribological properties of the coatings were evaluated using scratch testing, using two counter materials (1/16" balls of 100CR6 and Al₂O₃). To study the plastic deformation caused by the application of the load during the scratch measurements we used 3d profilometry. Finally, micro-Raman spectroscopy was employed to study any deformation-induced on the lattice and the chemical reactions produced, under the different loads, by the contact with the counterpart materials. The results show the TiSiN against alumina had the lower friction coefficient due to not showed reactive process on the surface for all load used just the movement of the Raman peak at lower wave numbers.

TR-ThP4 The Corrosion-Wear Mechanisms of CoCrMo Alloys Coated with TiAlN/TiAl Multilayer, Martin Flores, O. Jimenez, E. Rodriguez, Universidad de Guadalajara, Mexico, E. Andrade, Universidad Nacional Autónoma de México

The tribocorrosion phenomenon is present in biomedical alloys that are used in artificial implants to replace natural joints. This damage limits the service life of such implants, the hard coatings can improve the resistance to wear and corrosion. The multilayers of TiAlN/TiAl were deposited on CoCrMo alloys by magnetron sputtering. In this work we study the wear mechanism of the coated alloy and without multilayer in a simulated body fluid with an ion concentration similar to that in the human blood. The structure of coatings was studied by means of XRD and the composition by

RBS and EDS techniques. The tribocorrosion behavior of CoCrMo alloys alone and coated with TiAlN/TiAl multilayers was studied in simulated body fluid and distilled water. The tribocorrosion was performed using a tribometer with an geometry of ball on plate and reciprocating movement. The tests were conducted at 36 ± 1 °C of temperature. The loads used were 1N, 1.5, and 2N, the oscillating frequencies was 1Hz. The corrosion and tribocorrosion were studied using open circuit potential (OCP) in wear-corrosion tests and potentiodynamic polarizations in corrosion tests. In order to study the wear mechanisms, the topography and composition of worn surfaces were analyzed by means of SEM, EDS and profilometry. In the case of CoCrMo alloy it was found a transition from smooth wear to abrasive wear when the load was increased.

TR-ThP5 Improving the Surface Hardness of Plasma Nitrided 316L Stainless Steel, Petros Abraha, S. Mikashima, Meijo University, Japan

Stainless steels have very good corrosion resistance but the lower surface hardness poses marked limitation on the range of tribological applications that can be envisaged. Here plasma nitriding treatment was performed to modify the hardness without altering the corrosion resistance of austenitic 316L stainless steels.

In nitriding the 316L stainless steel, the passive CrO₂ layer that protects the surface from corrosion is removed first as it hinders the diffusion of nitrogen ions and atoms into the bulk of the stainless steel material. The removal of the passive layer was done by argon sputtering and the subsequent plasma nitriding was performed in electron beam excited plasma apparatus under nitrogen atmosphere for three hours. The apparatus was driven at an acceleration voltage of 100 volts and a beam current of 3 amperes. The sample temperature was held constant at 450 degree centigrade. Treated and untreated samples were characterized by means of morphological analysis, Vickers hardness measurements, and corrosion tests in NaCl solutions.

The results of our experiments show that nitriding treatments performed in primarily ion and neutral environs have increased hardness, slightly lower chrome concentration, and hence slightly higher quantity of rust. The measured hardness, chrome concentration, and quantity of rust for the non-treated samples were 230 Hv, 17 mass%, and 4 g/m², respectively. Ion nitriding in contrast largely increased the surface hardness of the stainless steel samples (more than 6 times), but decreased the corrosion resistance properties due to the CrN precipitation (15.8 mass %). Nevertheless nitriding treatments performed under neutral nitriding increased the surface hardness of the stainless steel samples (more than 3 times), avoid a large CrN precipitation (16.8 mass %) and rust quantity of 7.8 g/m² that is much lower than the 350 g/m² for ion nitriding. The above results indicate that stainless steels can be used as sliding or meshing mechanical parts in environments such as vacuum chambers and underwater machinery.

Tribology Focus Topic

Room: 303 - Session TR-FrM

Applications of Novel Materials in Tribology

Moderator: Barbara L. Mooney, United States Naval Academy

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

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

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

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

To demonstrate a technological application of such coatings, they were applied to the common lens material PC. Here, 40 nm or titania was deposited by liquid phase deposition² on a ten micrometer-thick PDMS "cushion" on top of the PC. In scratch tests, load to failure was increased by 5x relative to untreated PC and more than doubled relative to titania on PC without the cushion layer. These thin coatings had no detrimental effect on the optical properties of the PC. This work thus demonstrates, a simple, robust, and practical means of improving tribological properties in practical applications.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Zinc dialkylthiophosphates (ZDDPs) are lubricant additives used nearly universally in engine oils. Despite the generation of volatile phosphorous- and sulphur-containing compounds in the downstream gases that can reduce the working life of the catalytic converter, the unrivaled wear protection of ZDDPs makes them essential to lubricant performance. ZDDPs work by decomposing under tribological sliding to form nanoscale anti-wear films whose growth mechanisms are still poorly understood due to the complexity of the macroscopic multi-asperity sliding interfaces and the multiple chemical species involved (1). Greater understanding of the formation of these films is essential to enable rational design of more environmentally-friendly and energy-efficient engine oil formulations (2, 3). Here we report the development and application of a novel experimental approach using atomic force microscopy (AFM) for visualizing and quantifying the formation of ZDDP anti-wear films in-situ in a single asperity contact with

nanometer-scale spatial resolution. Experiments performed on iron-coated silicon surfaces at 80-140 °C in the presence of ZDDP containing polyalphaolefin oil show that thermal films grow on the substrate in the absence of tribological contact. These films are easily removed by sliding the tip at applied normal forces of only a few nanonewtons (contact pressure < 1.0 GPa). Continued sliding at higher normal loads (contact pressure ~ 2.0 -6.0 GPa) reveals the nucleation and growth of much more robust films with a pad-like lateral structure, similar to the morphology of anti-wear films formed by ZDDP in macroscopic contacts. The growth rate is nonlinear with time, and increases exponentially with temperature and contact pressure, in agreement with reaction rate theory. This is the first direct confirmation of asperity-level formation of such films, and the first quantification of the energetics of the tribofilm growth. Our findings provide new insights into the mechanisms of formation of ZDDP derived anti-wear films, enabling us to directly compare with atomistic predictions of pressure-induced cross-linking of zinc polyphosphates (4) and other possible proposed mechanisms (1).

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

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

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

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

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Bousser, E.: SE+NS+TR-TuM5, **3**
Brenner, D.: TR-ThA9, 7
Browning, J.: EN+EM+MN+NS+TR-MoA9, 1

— C —

Camps, E.: TR-ThP3, 8
Carpick, R.W.: TR+NS-ThM5, 5; TR-FrM10, 10;
TR-FrM6, 9
Chabal, Y.J.: EN+EM+MN+NS+TR-MoA3, 1
Cohen, H.: EN+EM+MN+NS+TR-MoA8, **1**
Cohen, S.R.: TR-FrM3, **9**
Coulter, K.: SE+NS+TR-TuM12, 4

— D —

Daniel, R.: SE+NS+TR-TuM11, 4
Dorman, J.: EN+EM+MN+NS+TR-MoA10, 1

— E —

Erdemir, A.: TR-ThA6, **7**
Eriguchi, K.: SE+NS+TR-TuM3, **3**

— F —

Fallet, M.: TR-FrM6, 9; TR-ThA8, **7**
Flores, M.: TR-ThP4, **8**
Frankel, D.J.: SE+NS+TR-TuM2, 3
Fujii, H.: EN+EM+MN+NS+TR-MoA11, 2
Fukuyama, A.: EN+EM+MN+NS+TR-MoA11, **2**

— G —

Gartstein, Y.: EN+EM+MN+NS+TR-MoA3, 1
Girolami, G.S.: TR-ThP2, 8
Girshevitz, O.: TR-FrM3, 9
Gosvami, N.N.: TR-FrM10, **10**
Gotlib-Vainshtein, K.: TR-FrM3, 9

— H —

Hahn, D.W.: TR+NS-ThM6, 5
Harrison, J.A.: TR+NS-ThM5, 5; TR-FrM6, 9; TR-
ThA8, 7
Hasegawa, S.: SE+NS+TR-TuM3, 3

Herath, N.: EN+EM+MN+NS+TR-MoA9, **1**
Huaranga, J.A.: TR-ThA10, 7
Hubbard, L.R.: SE+NS+TR-TuM1, **3**

— I —

Ikari, T.: EN+EM+MN+NS+TR-MoA11, 2

— J —

Jiang, Y.: TR+NS-ThM5, 5; TR-FrM6, **9**
Jimenez, O.: TR-ThP4, 8

— K —

Keating, P.L.: TR+NS-ThM5, 5
Keckes, J.: SE+NS+TR-TuM11, 4
Kim, W.-K.: TR+NS-ThM1, **5**
Klemberg-Sapieha, J.: SE+NS+TR-TuM5, 3
Knippenberg, M.: TR-ThA8, 7
Konicek, A.R.: TR-FrM10, 10
Krick, B.A.: TR+NS-ThM6, **5**

— L —

Lad, R.J.: SE+NS+TR-TuM2, 3
Lauter, V.: EN+EM+MN+NS+TR-MoA9, 1
Lee, P.M.: SE+NS+TR-TuM12, 4; TR-FrM8, **10**
Lin, J.: SE+NS+TR-TuM12, **4**

— M —

Malko, A.: EN+EM+MN+NS+TR-MoA3, 1
Mangolini, F.: TR-FrM10, 10
Martinu, L.: SE+NS+TR-TuM5, 3
Mikashima, S.: TR-ThP5, 8
Mikulski, P.: TR-ThA8, 7
Milne, Z.B.: TR-FrM6, 9
Mitterer, C.: SE+NS+TR-TuM11, **4**
Mohimi, E.: TR-ThP2, **8**
Muhl, S.: TR-ThP3, 8
Muscat, A.J.: SE+NS+TR-TuM1, 3

— N —

Nakano, Y.: EN+EM+MN+NS+TR-MoA11, 2
Nguyen, H.: EN+EM+MN+NS+TR-MoA3, 1
Nie, X.: TR-FrM4, 9
Nishioka, K.: EN+EM+MN+NS+TR-MoA11, 2
Noebels, M.: EN+EM+MN+NS+TR-MoA10, 1
Noma, M.: SE+NS+TR-TuM3, 3

— O —

Ono, K.: SE+NS+TR-TuM3, 3
Ozkan, T.: TR-ThP2, 8

— P —

Pastewka, L.: TR+NS-ThM10, 5; TR+NS-ThM13,
6; TR+NS-ThM3, **5**
Patscheider, J.: SE+NS+TR-TuM10, **4**
Pauca, K.: TR-ThA10, 7
Peng, W.: EN+EM+MN+NS+TR-MoA3, **1**
Pfadler, T.: EN+EM+MN+NS+TR-MoA10, 1
Polycarpou, A.A.: TR-ThP2, 8
Putnik, M.: EN+EM+MN+NS+TR-MoA10, 1

— R —

Restrepo, J.S.: TR-ThP3, **8**
Riedl, A.: SE+NS+TR-TuM11, 4
Robbins, M.O.: TR+NS-ThM10, **5**; TR+NS-
ThM13, 6
Rodriguez, E.: TR-ThP4, 8
Rowe, K.G.: TR+NS-ThM6, 5
Rupich, S.: EN+EM+MN+NS+TR-MoA3, 1
Ryan, K.E.: TR+NS-ThM5, **5**; TR-ThA8, 7

— S —

Saberi-Movahed, F.: TR-ThA9, **7**
Sampat, S.: EN+EM+MN+NS+TR-MoA3, 1
Sartory, B.: SE+NS+TR-TuM11, 4
Sawyer, W.G.: TR+NS-ThM6, 5
Schall, J.D.: TR-FrM5, **9**
Scheu, C.: EN+EM+MN+NS+TR-MoA10, 1
Schilowitz, A.M.: TR-FrM10, 10
Schmidt-Mende, L.: EN+EM+MN+NS+TR-
MoA10, 1
Schoeberl, T.: SE+NS+TR-TuM11, 4
Sell, J.C.: SE+NS+TR-TuM2, **3**
Sempstrott, P.J.: TR-ThP2, 8
Sharp, T.: TR+NS-ThM13, **6**
Shenderova, O.A.: TR-ThA9, 7
Shklover, V.: SE+NS+TR-TuM10, 4
Sobiech, M.: SE+NS+TR-TuM10, 4
Stefenelli, M.: SE+NS+TR-TuM11, 4
Stewart, D.M.: SE+NS+TR-TuM2, 3
Sugiyama, M.: EN+EM+MN+NS+TR-MoA11, 2
Sukenik, C.N.: TR-FrM3, 9
Sumant, A.V.: TR-ThA6, 7
Suzuki, H.: EN+EM+MN+NS+TR-MoA11, 2

— T —

Talledo, A.F.: TR-ThA10, **7**
Taylor, D.: EN+EM+MN+NS+TR-MoA3, 1
Thon, S.M.: EN+EM+MN+NS+TR-MoA1, **1**
Tjong, J.: TR-FrM4, 9
Turner, K.T.: TR+NS-ThM5, 5; TR-FrM1, **9**; TR-
FrM6, 9

— V —

Vahdat, V.: TR+NS-ThM5, 5

— W —

Walsh, K.: TR-ThP2, 8
Wang, G.: TR-FrM4, **9**
Wang, Z.L.: EN+EM+MN+NS+TR-MoA6, **1**
Wei, R.: SE+NS+TR-TuM12, 4
Weickert, J.: EN+EM+MN+NS+TR-MoA10, **1**
Wisnet, A.: EN+EM+MN+NS+TR-MoA10, 1

— Y —

Yablon, D.G.: TR-FrM10, 10
Yamashita, M.: SE+NS+TR-TuM3, 3

— Z —

Zauscher, S.: TR-ThA3, **7**