

# Tuesday Morning, October 31, 2017

## MEMS and NEMS Group

Room: 24 - Session MN+BI+EM+SS+TR-TuM

### Microelectromechanics: Relays to RF/Surfaces in Micro- and Nano- Systems

Moderators: Sushma Kotru, The University of Alabama,  
Roya Maboudian, University of California at Berkeley

#### 8:00am MN+BI+EM+SS+TR-TuM1 The Industrialization of MEMS through Materials Innovations, *Chris Keimel*, Menlo Micro INVITED

For the past 150 years, the mechanical relay was one of the original building blocks of electrical systems, for power electronics, controls, and even computing. With the introduction of the transistor in the middle of the 20<sup>th</sup> century, many industries were transformed with the introduction of ubiquitous, low-cost switches (solid-state) that could be manufactured by the billions with highly advanced equipment and manufacturing processes. Still today, many industries, especially power distribution and controls, are still not able to live with the tradeoffs of solid-state technologies (leakages, losses, lack of air-gap, thermal) and continue to employ large, slow, and costly mechanical relays which have evolved only slightly over the past 50+ years. The miniaturization of the mechanical relay through MEMS technology, coupled with materials innovations, will enable a new class of devices capable of connecting (wireless control) and controlling (distributed power) today's and the future's billions of automated electrical nodes.

We have developed electrostatically actuated MEMS relays capable of switching in ~3usec, sustaining more than 400V across its open contacts and controlling loads of 10s of watts to a few kilowatts. Ohmic MEMS switch with creep resistant metal alloy beams, and a highly reliable ruthenium contact has been developed based on methodical failure mode analysis taking into account material, mechanical and electrical constraints. The ohmic relays, when applied to RF applications, deliver multi throw configurations capable of <0.3dB insertion loss from DC to 3GHz combined with the ability to handle 25W of RF power.

A metal MEMS switch technology has been developed from the ground up through material, process, device, package and electronic integration innovations. The combination of fast microsecond switching speed and broadband (DC to RF) signal operation along with the ability to control amperes of current and sustain hundreds of volts across micron sized air gaps has enabled the miniaturization of the mechanical relay for broad ranging applications from wireless infrastructure to the Industrial IOT.

#### 8:40am MN+BI+EM+SS+TR-TuM3 Electron-Phonon Acoustoelectrics in MEMS, *Dana Weinstein*, Purdue University INVITED

The Acoustoelectric (AE) effect is a result of the interaction between free charge carriers and the electrical deformation potential produced by a propagating elastic wave in the piezoelectric. When an external DC electric field is applied across the semiconductor in the direction of the propagating wave, a drift velocity ( $v_d$ ) is imparted to the free carriers. If the drift velocity is slower than (or opposite to) the acoustic wave velocity ( $v_s$ ), the electrical deformation potential lags behind the strain wave. This phase lag not only decreases the acoustic wave velocity, but also transfers energy from the acoustic wave to the electrons, increasing the acoustic losses. When a sufficient DC field is applied to cause the drift velocity to exceed the acoustic wave velocity, the electrical deformation potential now leads the strain wave. This transfers energy from the electrons to the acoustic wave, resulting in an increased acoustic velocity and net acoustic gain [1,2,3,4].

A large body of work based on AE was established in the 1960s and 70s, resulting in a range of devices from phase shifters to correlators. With the development of new materials and new processing needs, there has been a recent resurgence of interest in this field, particularly for its amplifying and inherently non-reciprocal properties. Here, we discuss the implications of the AE effect for GHz frequency electromechanical signal processing. RF applications, linearity, and noise of the AE effect will be examined. Finally, benefits and limitations of prospective semiconductor/piezoelectric material systems will be discussed.

[1] J. H. McFee, "Transmission and Amplification of Acoustic Waves in Piezoelectric Semiconductors," *Phys. Acous. A*, vol. 4, 1-45 (1966).

[2] D. L. White, "Amplification of Ultrasonic Waves in Piezoelectric Semiconductors," *Journal of Applied Physics*, vol. 33, no. 8, pp. 2547-2554, Aug. 1962.

[3] B. K. Ridley, "Space charge waves and the piezo-electric interaction in 2D semiconducting structures," *Semiconductor Science and Technology*, vol. 3, no. 6, p. 542, 1988.

[4] G. S. Kino and T. M. Reeder, "A normal mode theory for the Rayleigh wave amplifier," in *IEEE Transactions on Electronic Devices*, vol. 18, no. 10, pp. 909-920, Oct. 1971.

#### 9:20am MN+BI+EM+SS+TR-TuM5 Autonomous Oscillations of a MEMS Resonator, *David Czaplewski*, Center for Nanoscale Materials, Argonne National Laboratory, *C. Chen, D. Lopez*, Argonne National Laboratory, *D.H. Zanette*, Centro Atomico Bariloche and Instituto Balseiro, *S.W. Shaw*, Florida Institute of Technology

Resonant MEMS and NEMS structures are used in a wide variety of applications including mass and force sensing, time keeping, and quantum information. For all MEMS and NEMS resonators, energy is lost every cycle of oscillation to the environment (modeled as a coupled bath). If this energy is not restored by an external source, the amplitude of the resonant motion will decrease toward zero. This well-known effect is commonly referred to as "ring-down". For linear resonators, the frequency of the resonator will remain constant and the amplitude will decrease exponentially while for non-linear resonators, the amplitude will decrease exponentially and the frequency will simultaneously decrease toward the linear response due to the amplitude-frequency (a-f) effect. However, we demonstrate a non-linear resonator that has constant frequency and an amplitude that does not decay for a given period of time (~0.1 s) after discontinuing the restoring energy to the system. We call this time "coherence time" because the amplitude and frequency of the oscillation does not decay when the restoring energy is removed. In essence, the resonator is autonomous during coherence time. Unfortunately or fortunately, this behavior does not violate the second law of thermodynamics. The behavior can be explained by looking at the entire system. We drive a non-linear MEMS resonator to a frequency where the primary mode couples with another internal mode. When the resonator is actively driven, the higher order mode receives energy from the primary mode. When the external energy is discontinued, this energy is restored back to the primary mode allowing the primary mode to continue to oscillate. However, once the energy stored in the higher order mode is depleted (its amplitude is near zero), the behavior of the primary mode begins to "ring-down". During this talk, I will show characteristics of the coupled modes including operation with constant frequency and a non-decaying amplitude for a period of time with no drive.

#### 9:40am MN+BI+EM+SS+TR-TuM6 Metallic Glass for MEMS Microphone Device, *MaiPhuong Nguyen*, WPI-Advanced Institute for Materials Research (WPI-AIMR)/ Micro System Integration Center ( $\mu$ SIC), Tohoku University, Japan, *J. Froemel*, WPI-Advanced Institute for Materials Research (WPI-AIMR), Tohoku University, Japan, *S. Tanaka*, Graduate School of Engineering/ Micro System Integration Center ( $\mu$ SIC), Tohoku University, Japan

Micro Electro-Mechanical Systems (MEMS) microphones have been extensively developed and introduced into mobile phones market with high performance such as high signal to noise ratio, good sensitivity, and power consumption and good reliability in terms of packages. Up to now, most studies have been focused on the improvement of sensitivity of microphone which is proportional to the compliance of the membrane. However, no significant progress has been achieved due to the limitation of material itself. Generally, single crystal and polycrystalline silicon based devices are brittle and fracture causing the interior defects during the fabrication processes. Therefore, the research of new materials to substitute polycrystalline silicon is necessary. Amorphous metals exhibit no grain boundaries, crystal defects and excellent mechanical properties such as fatigue free, large elastic limit, high strength, corrosion resistance which has been promising materials for MEMS devices such as micro-scanner, RF MEMS varactor, capacitive switch ... Metallic glasses are a kind of amorphous alloy exhibiting viscous flow at a certain temperature range so-called "supercooled liquid region". In the supercooled liquid region, metallic glasses can be easily produced through a variety of fast-cooling methods and have excellent mechanical formability. In addition, metallic glass thin films are easily prepared on Si or SiO<sub>2</sub> substrates by sputtering technique which is compatible with MEMS processes such as photolithography, dry or wet etching and lift off processing. Therefore, characterization and fabrication of metallic glasses films deposited by sputtering for MEMS microphone will be studied.

The CoTaB films with thicknesses in the range of 100 nm to several micrometers have been successfully deposited on thermal SiO<sub>2</sub> substrates by rf-sputter technique. The amorphous structure with smooth surface and negligible magnetic property was confirmed by TEM, AFM, XRD and SQUIDS measurement, respectively. The metallic glass behavior was investigated by DSC analysis which shows the glass transition and crystalline

temperature of 700 and 720.9 C, respectively. In addition, the mechanical properties such as stress, stress gradient and Young modulus have been studied by using pointer and cantilever structure. Co-based metallic glass exhibited tensile and compressive stress depending on sputter conditions, thicknesses as well as further treatment process. Additional results will be presented in detail at the conference with an emphasis on the dependence of the process conditions.

11:00am **MN+BI+EM+SS+TR-TuM10 Role of Surfaces in Assembly of Ceria Nanostructures, Sudipta Seal**, University of Central Florida **INVITED**

Cerium is a rare earth element of the lanthanide series with a fluorite lattice structure. The cerium atom can exist in either 3+ or 4+ states, and may alternate between the two in a redox reaction that is more pronounced in nanoparticles. However, the physicochemical properties of a nanocrystal assembly can be different from the properties of both the individual nanoparticles and the bulk phase. We have synthesized ceria nanoparticles in various medium and studied the self-assembly of particles to octahedral and star shaped nanostructure assembly. It was further identified that the concentration of Ce<sup>4+</sup> in nanoceria decreases over time, further controlling the surface chemistry. We will also highlight some of the key aspects of self-assembly of CeO<sub>2</sub> into nanorods. The surface area available and the orientation of crystallographic planes in ceria nanostructures highly regulate the catalytic property at nanoscale as evident by high resolution TEM. Further we discuss the role of Madelung energy and its relation to the catalytic activity, which is important in sensing and other analyte interactions. The surface chemistry or the ratio of Ce<sup>3+</sup>/Ce<sup>4+</sup> can be extensively modulated by the assembly process. At the end we report, the feasibility of a novel H<sub>2</sub>O<sub>2</sub> based electrochemical sensor that directly measures the current response of multivalent ceria in presence of H<sub>2</sub>O<sub>2</sub>. The fabricated sensor showed a picomolar range limit of detection while remaining insensitive to interfering species. Peroxide sensing is very important in biologically relevant oxidative stress in cells. It was observed that a lower ratio of Ce<sup>3+</sup>:Ce<sup>4+</sup> redox states elicits a greater current response towards H<sub>2</sub>O<sub>2</sub>. The detection of such electroactive analytes make it easier to detect using normal nanoparticle modified electrodes, thereby eliminating the use of organic mediators.

11:40am **MN+BI+EM+SS+TR-TuM12 Optimization and Nano-characterization of Electrostrictive Response of Gd-doped Ceria Actuators, Sidney Cohen, E. Mishuk, E. Makagon, E. Wachtel, K. Rechav, R. Popovitz-Biro, I. Lubomirsky**, Weizmann Institute of Science, Israel

Gd-doped ceria (GDC) recently attracted great interest due to its non-classical (non-Newnham) electrostrictive behavior. Although the material is well-known for its ionic conduction properties and use in solid-oxide fuel-cells, it also holds great promise for incorporation into MEMS devices because it is completely inert with respect to silicon compounds. The fact that GDC is lead-free is particularly appealing.

Here, we demonstrate fabrication and testing of membrane actuators formed with near 100% yield by a relatively simple, low temperature process. Preparation of these devices involves magnetron-sputtering of a thin film of GDC onto Si, and further processing using standard micromachining, resulting in free-standing membranes. Bridge and cantilever structures have been fabricated as well, to explore the possibility for diverse functional devices. The films were structurally characterized by electron microscopy and by x-ray diffraction, whereas electrical characterization was performed using impedance spectroscopy and cyclic voltammetry. These electrical tests revealed details of the conduction mechanism, role of the contacts, and charge-trapping.

Scanning probe microscopy was applied to quantitatively characterize the energetics and mechanics of the electromechanical response: Displacement of a circular membrane was measured by recording displacement of the cantilever probe under feedback as a function of frequency and applied voltage, and temporal Joule heating recorded using a scanning thermal probe. These measurements support calculations of heat-induced strain at high frequencies. These measurements showed that displacements obtained are sufficient for practical applications and provided insights on the factors controlling performance.

12:00pm **MN+BI+EM+SS+TR-TuM13 Sustainable Thermoregeneration of Plastrons on Superhydrophobic Surfaces, Tomer Simovich**, Ruhr-University Bochum, Germany, *J. Arnott*, The University of Melbourne, Australia, *A. Rosenhahn*, Ruhr-University Bochum, Germany, *R.N. Lamb*, Canadian Light Source, Canada

A popular and desirable function of superhydrophobic coatings is their remarkable ability to retain an entrapped layer of air, called a plastron, when submerged underwater. The drawback is that the air layer is short lived due to solvation into the surrounding liquid. Liquid gas extraction has been explored for the purpose of respiration through oxygen filtering or generation via chemical reaction. Manipulating solubility through temperature has been

attempted but due to its inefficiencies has not been developed further into functioning technologies. This paper introduces a novel method of extracting gas from water to generate enough air to permanently stabilize a plastron on superhydrophobic surfaces for sustained anti-fouling, rust resistance and drag reduction abilities. This method involves locally heating the liquid surrounding a superhydrophobic coating, reducing gas solubility causing the gas to migrate to the liquid-air interface. Due to the low surface energy of superhydrophobic coatings, nucleation of supersaturated gasses occurs preferentially at the coating interface, thereby replenishing the plastron. This requires a relatively low energy input, due to the small volume of water required to be locally heated combined with the small temperature differential induced between substrate and liquid. This process may be more environmentally sustainable in comparison to competing methods. With a constant supply of equilibrated water and minimal energy input, the plastron can survive indefinitely without need for the mechanical application of additional gas.

# Wednesday Afternoon, November 1, 2017

## Tribology Focus Topic

Room: 10 - Session TR+AS+HI+NS+SS-WeA

## Molecular Origins of Friction

**Moderators:** J. David Schall, Oakland University, Paul Sheehan, US Naval Research Laboratory

2:20pm **TR+AS+HI+NS+SS-WeA1 On the Stochastic Nature of Bonding in Contact: Simulations of Indentation and Sliding of DLC Tips on Diamond Surfaces.** *J. David Schall*, Oakland University, *R.A. Bernal*, University of Texas at Dallas, *Z. Milne*, University of Pennsylvania, *P. Chen*, *P. Tsai*, *Y.-R. Jeng*, National Chung Cheng University, Taiwan, Republic of China, *K.T. Turner*, *R.W. Carpick*, University of Pennsylvania, *J.A. Harrison*, United States Naval Academy

Contact at the nanoscale has important implications in the use of tip-based nanomanufacturing, data storage, and imaging with scanning probes. Tip wear reduces predictability in manufacturing and image quality such scanning probe applications. As a means to reduce wear, hard wear-resistant materials such as diamond-like carbon (DLC), ultra nanocrystalline diamond (UNCD) and amorphous carbon (a-C:H) have been used to coat scanning probe tips. Understanding of the behavior of these materials in contact is critically important towards their successful application. Recent studies using a TEM nanoindenter showed significant variation in both pull-in and pull-off forces obtained during the repeated indentation of a DLC tip on to a diamond surface. Furthermore, the pull-in and pull-off forces do not appear to be correlated. In this presentation, results from molecular dynamics simulations of a DLC tip on hydrogen terminated diamond surfaces will be presented. The tip was constructed with a structure and geometry similar to that of the tip used in experiment. The resulting simulations show that the pull-in force appears to be dominated by long range dispersion forces while the pull-off force is determined by the number of covalent bonds formed during the contact. For a given surface, the formation of bonds during indentation appears to be a stochastic process with multiple indents of the same tip at the surface same location showing a widely varying number of bonds formed. It is therefore hypothesized that the variation in pull-off forces observed in experiment are also related to the number of bonds formed across the tip-surface interface.

\*\*Supported by The National Science Foundation and the Air Force Office of Scientific Research

2:40pm **TR+AS+HI+NS+SS-WeA2 New Insights about the Fundamental Mechanisms of Friction of MoS<sub>2</sub>.** *John Curry*, Lehigh University, *M. Wilson*, *T.F. Babuska*, *M. Chandross*, Sandia National Laboratories, *H. Luftman*, *N.C. Strandwitz*, *B.A. Krick*, Lehigh University, *N. Argibay*, Sandia National Laboratories

Molybdenum Disulfide (MoS<sub>2</sub>) is a solid lubricant used widely in aerospace applications, capable of providing ultralow friction (coefficients,  $\mu < 0.01$ ) in inert environments such as the vacuum found in outer space. Research over the years has led to the development of MoS<sub>2</sub> nanocomposites that are less susceptible to the effects of environment and aging. Yet, the fundamental mechanisms responsible for environmental sensitivity and degraded friction behavior remain highly debated. Tribological experiments and molecular dynamics (MD) simulations were used to understand the evolution of friction behavior for MoS<sub>2</sub> coatings as a function of temperature, lattice commensurability and defect density. The oxidative resistance of MoS<sub>2</sub> coatings prepared with differing degrees of defect density and basal orientation was also assessed via high-sensitivity low-energy ion scattering (HS-LEIS) depth profiling, X-ray photoelectron spectroscopy (XPS), tribological experiments and MD. Through these findings, we discuss new connections between atomic-scale mechanisms and macro-scale friction behavior of this class of lubricant in a wide range of environments.

3:00pm **TR+AS+HI+NS+SS-WeA3 The Influence of Environmental Exposure and the Substrate on the Lubricating Properties of Two-Dimensional Materials.** *P. Gong*, University of Calgary, Canada, *Z. Ye*, Miami University, *L. Yuan*, *Philip Egberts*, University of Calgary, Canada

INVITED

The friction reducing properties of graphene has been shown to have a number of interesting properties, such as a dependence on the number of layers of the lubricant present, an exceptional dependence on the surface adhesion properties of the underlying substrate, and environmental stability. These properties have been attributed to its low mechanical strength to out-of-plane deformation, its innate thinness, and the influence of the environment on the surface energy. In this work, the friction reducing properties of graphene are examined using experiments and simulation. In

particular, the influence of surface energy and associated wettability of graphene are explored as a property that can influence the lubrication properties of graphene, but also friction hysteresis. While little to no variation in pull-off forces have been observed on varying numbers of graphene covering the surfaces in experiments, the impact of the variance of surface energy on friction, and in particular friction under humid environments, suggests that surface energy may have a stronger influence on graphene's friction reducing ability than suggested in previous work.

4:20pm **TR+AS+HI+NS+SS-WeA7 Fundamental Understanding of Interfacial Adhesion and Tribochemistry by Ab Initio Calculations.** *M.Clelia Righi*, University of Modena and Reggio Emilia, Italy **INVITED** Tribologically-induced chemical modifications of surfaces interacting with lubricant additives or other molecules present in the environment surrounding the sliding media can substantially change the adhesion and friction of materials in contact. Therefore, is highly desirable to understand how they take place. However, tribochemical reactions are difficult to monitor in real-time by experiments, which leaves a gap in the atomistic understanding required for their control.

We apply *ab initio* molecular dynamics to monitor chemical reactions involving common solid lubricants, namely molybdenum disulfide, graphene/graphite and carbon-based films, interacting with water molecules in the presence of mechanical stresses. Our simulations elucidate atomistic mechanisms relevant to understand the effects humidity on the lubricating properties of these materials.[1,2]

As second issue, we investigate the tribochemistry of sulfur, phosphorus and graphene on iron and discuss the role of metal passivation in reducing the interfacial adhesion and shear strength. We generalize the result by establishing a connection between the tribological and the electronic properties of interfaces. This adds a new piece of information for the ultimate understanding of the fundamental nature of frictional forces. [3,4]

[1] P. Restuccia, G. Levita and M. C. Righi *Graphene and MoS<sub>2</sub> interacting with water: a comparison by ab initio calculations* Carbon 107, 878 (2016).

[2] S. Kajita and M. C. Righi *A fundamental mechanism for carbon-film lubricity identified by means of ab initio molecular dynamics*, Carbon 103, 193 (2016).

[3] M. C. Righi, S. Loehlé, M. I. De Barros Bouchet, S. Mambingo-Doumbeand J. M. Martin *A comparative study on the functionality of S- and P-based lubricant additives by combined first principles and experimental analysis* RSC Advances, 6, 47753 (2016).

[4] P. Restuccia and M. C. Righi *Tribochemistry of graphene on iron and its possible role in lubrication of steel* Carbon 106, 118 (2016).

5:00pm **TR+AS+HI+NS+SS-WeA9 Friction Between 2D Solids during Lattice Directed Sliding.** *Paul Sheehan*, US Naval Research Laboratory, *CM. Lieber*, Harvard University

Nanometer-scale crystals of the 2D oxide molybdenum trioxide (MoO<sub>3</sub>) were formed atop the transition metal dichalcogenides MoS<sub>2</sub> and MoSe<sub>2</sub>. The MoO<sub>3</sub> nanocrystals are partially commensurate with the dichalcogenide substrates, being aligned only along one of the substrate's crystallographic axes. These nanocrystals can be slid only along the aligned direction and maintain their alignment with the substrate during motion. Using an AFM probe to oscillate the nanocrystals, it was found that the lateral force required to move them increased linearly with nanocrystal area. The slope of this curve, the interfacial shear strength, was significantly lower than for macroscale systems. It also depended strongly on the duration and the velocity of sliding of the crystal, suggesting a thermal activation model for the system. Finally, it was found that lower commensuration between the nanocrystal and the substrate increased the interfacial shear, a trend opposite that predicted theoretically.

5:40pm **TR+AS+HI+NS+SS-WeA11 Single Molecule Force Measurement: Mechanic and Symmetry Dependent Lateral Force.** *Yuan Zhang*, Argonne National Laboratory, *S. Khadka*, Ohio University, *B. Narayanan*, *A. Ngo*, Argonne National Laboratory, *Y. Li*, Ohio University, *B. Fisher*, *L. Curtiss*, *S. Sankaranarayanan*, *S.W. Hla*, Argonne National Laboratory

Mechanical properties of molecules adsorbed on materials surfaces are increasingly vital for the applications of molecular thin films as well as for the fundamental understanding of quantum friction. Here, we employ atomic/molecular manipulation schemes to investigate mechanic and symmetry dependent lateral diffusion processes of individual molecules on various substrates using a combined scanning tunneling microscope (STM) and q+ atomic force microscopy system at low temperature and in ultrahigh vacuum environment. Lateral force measurements of individual sexiphenyl,

an oligomer type molecule, exhibits an interesting friction behavior originated from the symmetry of the molecule-substrate system. We found ~160% increase in the lateral force during the diffusion of the molecule across a Ag(111) surface depending on the long molecular axis alignment on the surface. A comparison of the shape and symmetry dependent molecular diffusion process is realized by manipulating cobalt-porphyrin molecules on aAu(111) surface. The results are in full agreement with molecular dynamic simulations. In addition, we will also discuss atomic and molecular level force measurement using an STM tip, which opens simultaneous electronic, structural and force measurements at the single atom and molecule level.

# Thursday Morning, November 2, 2017

## Advanced Ion Microscopy Focus Topic

Room: 7 & 8 - Session HI+BI+NS+TR-ThM

## Advanced Ion Microscopy Applications

**Moderators:** Armin Golzhauser, Bielefeld University, Germany, Olga Ovchinnikova, Oak Ridge National Laboratory

8:00am **HI+BI+NS+TR-ThM1 Scanning Helium Atom Microscopy: Imaging with a Deft Touch**, *Paul Dastoor*, University of Newcastle, Australia **INVITED**

Delicate structures (such as biological samples, organic films for polymer electronics and adsorbate layers) suffer degradation under the energetic probes of traditional microscopies. Furthermore, the charged nature of these probes presents difficulties when imaging with electric or magnetic fields, or for insulating materials where the addition of a conductive coating is not desirable. Scanning helium microscopy is able to image such structures completely non-destructively by taking advantage of a neutral helium beam as a chemically, electrically, and magnetically inert probe of the sample surface. Here, we present scanning helium micrographs demonstrating image contrast arising from a range of mechanisms including, for the first time, chemical contrast observed from a series of metal-semiconductor interfaces [1]. The ability of neutral helium microscopy to distinguish between materials without the risk of damage makes it ideal for investigating a wide range of systems.

1. M. Barr, A. Fahy, J. Martens, A.P. Jardine, D.J. Ward, J. Ellis, W. Allison & P.C. Dastoor, "Unlocking new contrast in a scanning helium microscope", *Nature Communications*, **7**, 10189, (2016).

8:40am **HI+BI+NS+TR-ThM3 Biofilm Structure of Geobacter Sulfurreducens by Helium Ion Microscopy**, *Alex Belianinov*, Oak Ridge National Laboratory, *M. Halsted, M.J. Burch*, Oak Ridge National Laboratory, *S. Kim, S. Retterer*, Oak Ridge National Laboratory

Microbial communities form biofilms on material surfaces in a multitude of ecosystems, from the root hairs of a plant to the human gut. The hallmarks of an established biofilm include (1) the attachment of microbial cells to a surface, (2) production of extracellular polymeric substance, (EPS) (3) a complex structure or "architecture," and (4) the ability to exchange genetic information between cells. [1] *Geobacter sulfurreducens* forms unique, electrically conductive biofilms, a property that can be exploited in production and design of microbial fuel cells. In this work, examine biofilm formation, and biofilm properties of *Geobacter sulfurreducens* using a Scanning Electron Microscope (SEM) as well as a Helium Ion Microscope (HIM).

SEM is a high-resolution imaging technique used for characterization of a broad variety of materials. However, in order to image highly insulating, soft biological materials, the samples must be coated for charge compensation. These (typically) metallic coatings create a homogenous surface and may cloak true biological behavior and material contrast in the micrograph. In the case of *Geobacter sulfurreducens*, metal coating precludes detailed investigation of microbial attachment, presence of EPS, and fine surface details that may elucidate the mechanisms behind architecture formation and genetic material exchange.

Recently introduced HIM, offers more flexibility in investigating biological samples, as highly insulating sample can be imaged *sui generis*, without the use of a conductive coating. [2] This opens new pathways to capturing high resolution spatial details of biofilm formation and biofilm properties. Furthermore, high-resolution HIM imaging reveals true surface details of *Geobacter sulfurreducens*, such as flagella or pilin typically inaccessible by SEM. Finally, the effects of different sample preparation strategies for SEM and HIM will be illustrated and discussed.

References:

[1] I. Donlan, R. M. "Biofilms: Microbial Life on Surfaces." *Emerging Infectious Diseases*, 8(9), 881–890, 2002

[2] Joens, M. S., Huynh, C., Kasuboski, J. M., Ferranti et. al. "Helium Ion Microscopy (HIM) for the imaging of biological samples at sub-nanometer resolution." *Scientific Reports*, 3(3514), 2013

Acknowledgements:

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9:00am **HI+BI+NS+TR-ThM4 Channeling via Transmission He Ion Microscopy**, *Christoph Herrmann*, Simon Fraser University, Canada, *S.A. Scott, M. Lagally*, University of Wisconsin-Madison, *K. Kavanagh*, Simon Fraser University, Canada

The spatial coherence of focussed helium (He) ion beams is significant. The He ion source is atomic size (W filament tip) and the resolution from scanning probe, ion-induced secondary electron images is sub 1 nm. Scanning transmission images with atomic resolution are theoretically predicted. We have been experimenting with a digital camera located underneath the sample stage and tilt cradle of our instrument (Zeiss Nanofab). The camera consists of an array of Si p-i-n diodes (55  $\mu\text{m}$  square pixels) that allow direct detection of single He ions and atoms (20 keV - 40 keV). We have previously reported that the beam intensity profiles are uniformly distributed, as expected from the small de Broglie wavelength (80 fm), with a half angle convergence of 2 mrad.[1] At beam currents in the pA range the detector count rate was consistent with one count per He ion or atom. In this talk, we will present results that indicate planar channeling in single crystalline Si (100) membranes (25 nm - 75 nm thick). The transmission intensity as a function of position depends on the beam incidence angle, and beam energy, with random incidence profiles consistent with monte carlo scattering and range calculations (SRIM). The peak in transmission as a function of incidence angle has a half angle width of 1° at 25 kV. These results will be compared with theoretical calculations based on impact factors at low energies. Channeling experiments with other thin crystalline materials including graphite and MgO will be discussed. **Acknowledgements:** We thank Norcada Inc. (Edmonton) for supplying Si (100) 50 nm thick membranes; NSERC, CFI/BCKDF, 4DLABs for funding. [1] K.L. Kavanagh and C. Herrmann, Direct He Detection for Transmission Helium Ion Microscopy, *Microsc. Microanal.* submitted 2017.

9:20am **HI+BI+NS+TR-ThM5 Rapid Imaging of Nano-Porous Catalyst Particles Via Helium Ion Microscopy**, *M.J. Burch, A.V. Ievlev, Holland Hysmith*, Oak Ridge National Laboratory, *K. Mahady, P.D. Rack*, University of Tennessee, *L. Luo*, ExxonMobil Chemical Company, *A. Belianinov*, Oak Ridge National Laboratory, *S. Yakovlev*, ExxonMobil Chemical Company, *O.S. Ovchinnikova*, Oak Ridge National Laboratory

Porous materials are some of the most important modern day material systems, as the pore structure defines many materials applications and functionality. The pore structure of catalyst precursor particles, in particular, is of great importance to the catalyst community, as this pore structure dictates the efficiency and efficacy of grown polymers. However, despite the importance of these materials systems, there are few techniques to analyze pore size and structure. The most common technique is gas absorption, where the amount of gas absorbed and desorbed from a known amount of material is tracked and the average pore volume and size can be extracted. However, the technique is heavily dependent on sample quality and which fitting model is used to calculate volume and size. In addition, the technique is quite slow, where generally at most a single sample can be analyzed a day.

In this work, we demonstrate a novel technique to directly image and quantify pore size in nano-porous catalyst precursor particles via helium ion microscopy. We demonstrate the technique by directly imaging the surface pore structure of SiO<sub>2</sub> precursor catalyst particles with helium ion microscopy. Using modern day data analytics, we created an automated routine to extract pore size and distributions. We show that our HIM based technique shows comparable data to the industry standard gas absorption technique, within a 5 percent difference between the techniques of a known porous samples.

Further, to determine the effect of the helium beam on the surface of the SiO<sub>2</sub> particles, we simulate the beam interaction between porous SiO<sub>2</sub> particles and the helium beam. At low ion doses the surface modification by the ion beam is quite negligible, where at higher ion doses, significant surface modification is observed.

In conclusion, we've demonstrated a novel technique to directly visualize and quantify nano-pore size and structure in SiO<sub>2</sub> that yields complimentary data to gas absorption.

**Acknowledgements**

This work was conducted at the Center for Nanophase Materials Sciences, which is a Department of Energy (DOE) Office of Science User Facility. The users acknowledge the ExxonMobil Chemical Company for funding.

9:40am **HI+BI+NS+TR-ThM6 Ion Beam Induced Current Measurements of Solar Cells with Helium Ion Microscopy**, A. Belianinov, S. Kim, Ryan Cannon, M.J. Burch, S. Jesse, O.S. Ovchinnikova, Oak Ridge National Laboratory

The scanning electron microscope (SEM) is a versatile high-resolution microscopy tool, and perhaps the most widely used imaging platform across many engineering and scientific fields [1]. Within the last decade, another microscopy technique based on a gaseous field ionization source, utilizing Helium and Neon ions has been introduced [2]. While the popularity of the SEM is hardly challenged by the Helium Ion Microscopy (HIM), there are instances when imaging with ions offers significant advantage as opposed to imaging with electrons. In principle, both HIM and the SEM share many similarities, for example, a HIM operating at 40 keV will generate ions with velocity comparable to SEM operating at 5 keV. However, due to much higher stopping power of ions, as compared to electrons, ion based secondary electron (iSE) will be higher. Also, as a result, there is little ion backscattering, and consequently, the concentration of the ion-generated iSE2 (additional secondary electron generated by SE interaction within the material) is usually insignificant.

In this work, we exploit small interaction volumes in the HIM, and take advantage of the lower iSE2 yield, and positively charged helium ions to map ion beam induced current (IBIC) in solar cell materials. Similar studies, using electrons, have visualized induced current profiles at grain profiles in polycrystalline solar cells, and in silicon [3, 4]. Furthermore, broad ion sources have been utilized in conjunction with scanning probe systems in the past to map out current changes in FinFETs [5]. We are interested in utilizing the HIM to map current at the nanoscale near p-n junctions in CdTe to elucidate differences in contrast captured by the ion beam induced current, as opposed to the electron beam induced current. These findings will illustrate the peculiarities of ionic transport in these solar cell materials, and will evaluate the HIM technology as a potential quality control tool.

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- [3] Donolato, C., Journal of Applied Physics, 54 (3), 1314-1322, 1983
- [4] Chen, J., et. al., Journal of Applied Physics, 96(10), 5490-5495, 2004
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11:00am **HI+BI+NS+TR-ThM10 Writing Magnetic Domains with a Helium Ion Microscope**, Daniel Emmrich, Bielefeld University, Germany, A. Gaul, D. Holzinger, A. Ehresmann, University of Kassel, Germany, F. Karimian, M. Klug, J. McCord, Kiel University, Germany, A. Beyer, A. Götzhäuser, Bielefeld University, Germany

Microscopes based on gas field ion sources offer surface-sensitive, high resolution imaging and state of the art nano-machining.<sup>1</sup> It was further shown that light ions like helium or neon enable a modification of the magnetic properties, e.g., turning thin films from paramagnetic to ferromagnetic state, without significant sputtering.<sup>2</sup>

In this work, two-dimensional ion bombardment induced magnetic patterning (IBMP)<sup>3</sup> is demonstrated with a helium ion microscope to create magnetic domains in an exchange biased thin film system. Such a system consists of a thin ferromagnetic layer coupled to an underlying antiferromagnet. Low dose helium ion irradiation at an energy of 15 keV in an external magnetic field leads to a new, remanent magnetization direction, determined by the external magnetic field. By subsequently patterning the sample in differently orientated external magnetic fields, complex magnetic domain patterns such as chiral structures can be written. Based on magnetic force microscopy and optical Kerr microscopy, we will discuss the achievable resolution as well as the shapes of different artificial magnetic domains.

<sup>1</sup>G. Hlawacek and A. Götzhäuser (eds), Helium Ion Microscopy (Springer International Publishing, Switzerland, 2016).

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<sup>3</sup>A. Gaul, S. Hankemeier, D. Holzinger, N.D. Mücklich, P. Staack, R. Frömter, H.P. Oepen, and A. Ehresmann, Journal of Applied Physics 120, 33902 (2016).

11:20am **HI+BI+NS+TR-ThM11 Characterisation of Nanomaterials on the Helium Ion Microscope using Correlative Secondary Electron and Mass Filtered Secondary Ion Imaging**, J.-N. Audinot, D.M.F. Dowsett, F. Vollnhals, T. Wirtz, Luxembourg Institute of Science and Technology (LIST), Luxembourg, John A. Notte, Carl Zeiss Microscopy, LLC

In order to add nano-analytical capabilities to the Helium Ion Microscope, we have developed a Secondary Ion Mass Spectrometry (SIMS) system specifically designed for the Zeiss ORION NanoFab [1-3]. SIMS is based on the generation and identification of characteristic secondary ions by irradiation with a primary ion beam (in this case helium or neon). It is an extremely powerful technique for analysing surfaces owing in particular to its excellent sensitivity (detection limits down to the ppb are possible, so that SIMS can be used to detect both major and trace elements), high dynamic range (a same signal can be followed over several orders of magnitude), high mass resolution and ability to differentiate between isotopes.

In SIMS, the typical interaction volume between the impinging ion beam and the sample is around 10 nm in the lateral direction. As the probe size in the HIM is substantially smaller (both for He and Ne), the lateral resolution on the integrated HIM-SIMS is limited only by fundamental considerations and not, as is currently the case on commercial SIMS instruments, the probe size [4,5]. We have demonstrated that our instrument is capable of producing elemental SIMS maps with lateral resolutions down to 12 nm [3-5].

Furthermore, HIM-SIMS opens the way for in-situ correlative imaging combining high resolution SE images with elemental and isotopic ratio maps from SIMS [4,5]. This approach allows SE images of exactly the same zone analysed with SIMS to be acquired easily and rapidly, followed by a fusion between the SE and SIMS data sets.

In this talk, we will present a number of examples taken from various fields of materials science (battery materials, solar cells, micro-electronics, coatings) and life science (nanoparticles in creams and biological tissues) to show the powerful correlative microscopy possibilities enabled by the integrated HIM-SIMS instrument.

- [1] T. Wirtz, N. Vanhove, L. Pillatsch, D. Dowsett, S. Sijbrandij, J. Notte, Appl. Phys. Lett. 101 (4) (2012) 041601-1-041601-5
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## Tribology Focus Topic

**Room: 10 - Session TR+AC+TF+VT-ThM**

## Lubricant, Coatings, and Biotribology

**Moderator:** J. David Schall, Oakland University

8:00am **TR+AC+TF+VT-ThM1 Superlubricity of Hard Compliant Carbon Coatings with Green Lubricants: Role of Surface Chemistry and Structural Changes**, Maria-Isabel De Barros Bouchet, Ecole Centrale de Lyon - LTDS, France **INVITED**

Reduction of energy loss by mechanical friction has been strongly required in recent years for improving fuel efficiency especially for automotive engine. Even at a modest rate, it is of primary importance to reduce parasitic energy losses and provide environmental sustainability. An approach to achieve this target is the development of new lubrication technologies, combining new lubricant formulations and cutting-edge coatings transferable to industrial applications. Since superhard carbon material like tetrahedral amorphous carbon (ta-C) and Nano-Crystalline Diamond (NCD) coatings combine both crucial properties, high hardness with an ultra-smooth surface roughness, they have attracted a growing interest in the last decade. While the friction coefficient is generally extremely high under ultra high vacuum conditions, in the earlier years we have discovered the ability of these coatings to be lubricated by selected biodegradable green molecules like fatty acids, glycerol mono-oleate GMO and polyols, as well as their mixture with synthetic base oil such as Poly-Alpha Olefines (PAO). Some of these compounds are able to lubricate ta-C and NCD coatings with a friction coefficient below 0.01 (so-called superlubricity) in thin-film EHL/mixed regime and below 0.03 in severe boundary regime without significant wear<sup>1</sup>. As this case of superlow friction is extremely promising for many applications fields, the related mechanism has been investigated and a special attention has been paid to the surface chemistry and structural changes of the

carbon coatings. By coupling advanced extreme surface analyses (PES and XANES), we show that the mechanism of friction reduction is related to the tribo-formation of quasi-2D planar graphene-like structures at the top of the colliding asperities (thickness about 1 nm). Eventually, the graphene can be slightly oxidized by the OH-groups coming from the tribo-decomposition of the lubricant molecules trapped between asperities. Moreover, the rubbed sub-surface is enriched with sp<sup>2</sup>-hybridized carbon, such as in a soft a-C material, during the friction. These strong structural changes certainly ease the tribochemical-formation of the carbon rings present in the graphene-like structure as pointed out by atomistic computer simulations.

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8:40am **TR+AC+TF+VT-ThM3 Role of Deuterium and Hydrogen in the Physical Understanding of Nano-friction in a-C:H/D Thin Films**, *F.G. Echeverrigaray, S.R. Sales de Mello, A.F. Michels, UCS, Brazil, F. Alvarez, UNICAMP, Brazil, Carlos Figueroa, UCS, Brazil*

The friction phenomenon is a complex manifestation of the nature. In spite of phenomenological laws can describe the friction force at different scales, the fundamental physical understandings of such a phenomenon do not have consensus. Phenomena such as phononic, electronic, magnetic, and also electrostatic effects and models were developed in order to explain the meta- and nano-friction behavior of materials. In this work, we report the friction behavior of a diamond spherical dome sliding on different amorphous carbon thin films containing different amounts of hydrogen and/or deuterium inspecting at the meta-nanoscale indentation. Two important situations are reported. Firstly, for samples where hydrogen was replaced by deuterium in the thin film bulk, the friction coefficient decreases for increasing deuterium included in the carbon underneath structure. Secondly, for samples where hydrogen content is increased on the surface, the friction coefficient decreases with the increasing of the ratio H/C at the surface. In this paper, we discuss two different physical mechanisms describing these peculiar experimental results: dissipation effects associated with phonon coupling and van der Waals forces contributions coexisting and determining the friction behaviour of a-C:H/D for the cited studied situations.

9:00am **TR+AC+TF+VT-ThM4 Imaging X-Ray Absorption Spectroscopic Investigation of the Mechanisms Behind the Environmental Dependence of the Tribological Properties of Amorphous Carbon Surfaces**, *Filippo Mangolini, University of Leeds, UK, M. Koshigan, Ecole Polytechnique Montréal, Canada, M.H. Van Benthem, J.A. Ohlhausen, Sandia National Laboratories, J.B. McClimon, J. Hilbert, University of Pennsylvania, J. Fontaine, Ecole Centrale de Lyon, France, R.W. Carpick, University of Pennsylvania*

Among the variants of diamond-like carbon films developed for the ever-increasing performance and durability requirements of tribo-mechanical applications, silicon oxide-containing hydrogenated amorphous carbon (a-C:H:Si:O) is of interest as it exhibits good tribological performance across a broader range of environments compared to hydrogenated amorphous carbon, and higher thermo-oxidative stability. However, the scientific basis for this improved behavior is not established. In this work, we develop a fundamental understanding of the structural transformations occurring in a-C:H:Si:O when sliding against steel in different environments (from high vacuum to controlled hydrogen and oxygen pressures). The results of tribological experiments revealed that upon increasing the oxygen pressure in the experimental chamber from 10 mbar to 1000 mbar, the coefficient of friction increased from 0.02±0.01 to 0.06±0.01, whereas upon increasing the hydrogen pressure from 50 mbar to 2000 mbar, the coefficient of friction decreased from 0.08±0.01 to 0.02±0.01. The subsequent near edge X-ray absorption fine structure (NEXAFS) spectroscopic measurements and X-ray photoelectron spectroscopy (XPS) analyses provided insights into the structural transformations and chemical reactions occurring in a-C:H:Si:O upon sliding. Independently of the gas, a stress-induced conversion from sp<sup>3</sup>- to sp<sup>2</sup>-bonded (disordered) C-C bonds occurs. When sliding in hydrogen, the newly-generated, strained sp<sup>2</sup> carbon layer reacts with hydrogen molecules to form a hydrogenated amorphous carbon interfacial material. Upon increasing the hydrogen pressure, the fraction of C-H bonds increases in the near-surface region of the wear tracks formed on a-C:H:Si:O. This is proposed to progressively lower the shear strength of the material at the sliding interface, thus resulting in a decrease of friction with hydrogen pressure. When sliding in oxygen, the dissociative reaction of oxygen molecules with strained sp<sup>2</sup> C-C bonds leads to the formation of C=O groups. Additionally, increasing the oxygen pressure during tribological testing leads to an increase in oxygen concentration in the near-surface region of a-C:H:Si:O together with an increase in the fraction of Si atoms in high oxidation states. These surface chemical changes and structural transformations are proposed to increase

friction with oxygen pressure by progressively increasing the shear strength of the material generated at the sliding interface.

9:20am **TR+AC+TF+VT-ThM5 Structure Evolution in Tribological Interfaces Studied by Multilayer Model Alloys**, *Martin Dienwiebel, E. Cihan, Karlsruhe Institute for Technology (KIT), Germany* **INVITED**

During sliding of surfaces the near surfaces undergo significant changes in terms of topography, composition and microstructure and a so-called “third body” or “tribomaterial” forms which differs strongly from the bulk materials in terms of topography, composition and microstructure. Initially we use multilayer model alloys of an Au/Ni layer system to study effects of grain size on steady-steady friction by varying the layer spacing and the number of layers. Experiments are performed in a UHV microtribometer, the analysis of microstructure before and after tribological stressing is done by FIB and STEM and the chemistry is investigated by XPS. During sliding of surfaces the near surfaces undergo significant changes in terms of topography, composition and microstructure and a so-called “third body” or “tribomaterial” forms which differs strongly from the bulk materials in terms of topography, composition and microstructure. Initially we use multilayer model alloys of an Au/Ni layer system to study effects of grain size on steady-steady friction by varying the layer spacing and the number of layers. Experiments are performed in a UHV microtribometer, the analysis of microstructure before and after tribological stressing is done by FIB and STEM and the chemistry is investigated by XPS.

11:00am **TR+AC+TF+VT-ThM10 Carbon, Carbon Everywhere, from Catalysts to Hip Implants**, *Laurence Marks, Northwestern University* **INVITED**

Friction is a pervasive problem, by some estimates consuming about 5% of the GDP of the economies of the developed world, and a recent analysis has indicated that about one third of the fuel energy in automobiles goes to overcoming frictional losses. While the importance of minimizing friction can be traced back at least as far as the tomb of Tehuti-Hetep, circa 1880 B.C, where a man can be seen pouring a lubricant to assist moving a statue, there are still many unknowns in the field of tribology which encompasses friction as well as other critical processes such as wear and lubrication. For many of the phenomena in tribology there are still numerous unknowns. When it comes to biological systems most work to date has assumed that different mechanisms are taking place than occur for inorganic systems. While there are differences, there are also significant similarities particularly in implants when inorganic and biological meet. We have recently shown that for metal implants in-vivo the same type of graphitic materials that appear in many areas ranging from heterogeneous catalysis to oil lubrication are present. Beyond just lubrication, corrosion of these materials is not special to biological systems, but has strong similarities to established factors such as grain boundary precipitation and a significant role for molybdenum as reducing the occurrence of breakdown of the protective oxide film via complex processes involving solute trapping. These and related recent results will be described.

11:40am **TR+AC+TF+VT-ThM12 Tribology of Cellular Interfaces**, *Angela Pitenis, J.M. Uruña, S.M. Hart, T.T. Hormel, C.S. O'Bryan, S.L. Marshall, K.D. Schulze, P.P. Levings, T.E. Angelini, W.G. Sawyer, University of Florida* **INVITED**

Human health, mobility, and quality of life critically hinge on the body's ability to provide adequate lubrication between most contacting and sliding biological interfaces. Soft, aqueous, and mucinated biopolymer networks lining all moist epithelia enable the body to provide lubricity over a wide range of contact pressures and sliding speeds. The exquisite slipperiness and softness of biological sliding interfaces present significant experimental challenges for fundamental studies on their tribological performance. Physiological contact pressure conditions must be matched in vivo, ex vivo, and in vitro studies that aim to acquire physiologically-relevant friction measurements. While biotribological investigations using living cells, cell layers, and tissues necessitate low contact pressure measurements, such studies frequently rely on the application of low forces to achieve accommodating contact pressures (kPa range), and traditional methods can decrease the contact area below a physiologically-relevant threshold. The softness of a cell layer (E ~ 10 kPa) provides an order-of-magnitude estimate for the amount of mechanical pressure that may be applied to cells during tribological testing; contact pressures about 5 kPa and shear stresses in excess of 200 Pa are sufficient to wreak significant damage to a cell layer. Recently, direct contact tribological experiments on a living cell layer without incurring any measurable cell death in the sliding path has become possible through the application of a soft, thin, spherically-capped membrane hydrogel probe. With this experimental configuration, in vitro tribological experiments were performed against a monolayer of mucin-producing human corneal epithelial cells (hTCEpi) for 10,000 reciprocating cycles at physiologically-relevant contact pressures and challenging sliding speeds. The gel-cell sliding interface under applied normal loads of ~ 200 μN resulted in measured

friction coefficients of  $\mu \sim 0.06$  and achieved shear stresses on the order of 60 Pa, which is below the critical shear stress for inducing cell death; excellent cell survival rates ( $\sim 99.8\%$ ) were measured after extended duration tribological experimentation.



# Thursday Afternoon, November 2, 2017

## Advanced Ion Microscopy Focus Topic

Room: 7 & 8 - Session HI+NS+TR-ThA

### Novel Beam Induced Surface Analysis and Nano-Patterning

**Moderators:** Anne Delobbe, Orsay Physics, Shinichi Ogawa, National Institute of Advanced Industrial Science and Technology (AIST)

#### 2:20pm HI+NS+TR-ThA1 Multimodal Chemical Imaging of Nanoscale Interfacial Phenomena on a Combined HIM-SIMS Platform, *Olga Ovchinnikova*, Oak Ridge National Laboratory **INVITED**

The key to advancing energy materials is to understand and control the structure and chemistry at interfaces. However, significant gaps hamper chemical characterization available to study and fully comprehend interfaces and dynamic processes; partly due to the lack of breadth of necessary information, as well as its scattered nature among a multitude of necessary measurement platforms. Multimodal chemical imaging transcends existing analytical capabilities for nanometer scale spatially resolved interfacial studies, through a unique merger of advanced helium ion microscopy (HIM) and secondary ion mass spectrometry (SIMS) techniques. In this talk I will discuss how to visualize material transformations at interfaces, to correlate these changes with chemical composition, and to distill key performance-centric material parameters using a multimodal chemical imaging approach on a combined HIM-SIMS system. Particular attention will be focused on how to use the HIM-SIMS to study the role of ionic migration on the photovoltaic performance, or alternatively whether the ionic migration plays a positive or negative role in determining superior photovoltaic performance in organic-inorganic perovskites (HOIPs). I will discuss how synthesizing perovskite on custom substrates effect active chemical agents in materials and understand how interfaces in materials affect the local chemistry, specifically, key energy related parameters such as electron and ion motion and their re-distribution. Overall, multimodal chemical imaging on a combined HIM-SIMS platform offers the potential to unlock the mystery of active interface formation through intertwining data analytics, nanoscale elemental characterization, with imaging; to better grasp the physical properties of materials and the mechanistic physics-chemistry interplay behind their properties.

#### Acknowledgements

This work was conducted at the Center for Nanophase Materials Sciences, which is a Department of Energy (DOE) Office of Science User Facility

#### 3:00pm HI+NS+TR-ThA3 Characterizing Surface Immobilized Antibodies using ToF-SIMS and Multivariate Analysis, *N.G. Welch*, CSIRO Manufacturing, Australia, *R.M.T. Masiona*, La Trobe University, Australia, *J.A. Scoble*, *B.W. Muir*, CSIRO Manufacturing, Australia, *Paul Pigram*, La Trobe University, Australia

Antibody attachment, orientation and function at the solid interface are critical for the sensitive detection of biomolecules during immunoassays. Correctly oriented antibodies with solution-facing antigen binding regions have improved antigen capture in comparison with randomly oriented antibodies. Direct characterization of oriented proteins with surface analysis methods still remains a challenge. Surface sensitive techniques, however, such as Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) provide information-rich data that can be used to probe antibody attachment, orientation, denaturation and related characteristics.

Diethylene glycol dimethyl ether plasma polymers (DGpp) functionalized with chromium (DGpp+Cr) have improved immunoassay performance that is indicative of preferential antibody orientation. ToF-SIMS data from proteolytic fragments of anti-EGFR antibody bound to DGpp and DGpp+Cr have been used to construct artificial neural network (ANN) and principal component analysis (PCA) models indicative of correctly oriented systems. Whole antibody samples (IgG) tested against each of the models indicate preferential antibody orientation on DGpp+Cr. Cross-reference between ANN and PCA models yield 20 mass fragments associated with F(ab')<sub>2</sub> region representing correct orientation, and 23 mass fragments associated with the Fc region representing incorrect orientation. The mass fragments have been compared with amino acid fragments and amino acid composition in F(ab')<sub>2</sub> and Fc regions. A ratio of the sum of the ToF-SIMS ion intensities from the F(ab')<sub>2</sub> fragments to the Fc fragments demonstrated a 50% increase in intensity for IgG on DGpp+Cr as compared to DGpp.

This systematic data analysis methodology offers new opportunities for the investigation of antibody orientation on a range of substrates. It also yields

good results for the characterization of antibody denaturation and for determining limits of detection.

#### 4:00pm HI+NS+TR-ThA6 Single-nanometer Functional Graphene Devices Patterned with Helium Ion Beam, *Hiroshi Mizuta*, *M.E. Schmidt*, *T. Kanzaki*, Japan Advanced Institute of Science and Technology (JAIST), Japan, *S. Ogawa*, National Institute of Advanced Industrial Science and Technology (AIST), Japan, *M. Muruganathan*, Japan Advanced Institute of Science and Technology (JAIST), Japan **INVITED**

The bombardment of specimen by accelerated ions causes implantation and surface sputtering. The latter can be employed to create structures with sub-10 nm dimensions. This precision is demonstrated in electrically contacted and suspended graphene layers by a Helium ion microscope (HIM). 5 nm wide monolayer graphene, suspended above a pore and milled by HIM, had been demonstrated [1]. However, the physical properties of such a ribbon cannot be investigated in such a device architecture due to lack of electrical contacts. Recently, we demonstrated a ~6 nm wide suspended GNR and reported on the room temperature electrical characteristics. A wide range of drain current, at which current suppression occurs, has been observed [2]. However, that device was based on exfoliated grapheme, which makes it necessary to individually design the structures, and the yield is typically small.

Here, we report on the large-array processing of 100 nm wide monolayer CVD based suspended graphene structures by HIM. The structures are prepared by electron-beam lithography and thin-film processing. Before HIM milling, the graphene is released by buffered hydrofluoric acid etching and critical point drying. Annealing in H<sub>2</sub>/Ar atmosphere is used to remove the resist contamination.

We will first discuss results of fabricating suspended GNRs with constriction milled with HIM (30 keV acceleration voltage, 1.1x10<sup>18</sup> ion/cm<sup>2</sup>). The GNRs with sub-10-nm constriction are successfully patterned, and the electrical conduction is measured as function of temperature. We will discuss the milling results and electrical characterization in detail along with their potential impact on the performance of graphene-NEMS-based single-molecular detection [3]. We will then report on the recent progress in preparing arrays of nanopores in graphene by HIM. 9x9 arrays with pitch of ~9 nm are successfully realized with a dose of 6.5x10<sup>18</sup> ions/cm<sup>2</sup>. Arrays of pores spanning a complete suspended ribbon with a pitch of ~18 nm are demonstrated as well, and we will discuss the impact of such periodic structure on the electrical and thermal (phononic) transport for nanoscale heat phonon engineering.

**Acknowledgements:** T. Iijima is acknowledged for the usage of the HIM at AIST SCR Station. This research was supported through the Grant-in-Aid for Scientific Research KAKENHI 25220904, 16K13650, 16K18090 from JSPS and COI program of the Japan Science Technology Agency.

**References** [1] D. Pickard and L. Scipioni, "Graphene Nano-Ribbon Patterning in the ORION® PLUS," Zeiss application note, 2009. [2] M. E. Schmidt *et al.*, 63<sup>rd</sup> JSAP Spring Meeting (2016) [3] J. Sun *et al.*, Science Advances 2(4), e1501518 (2016)

#### 5:00pm HI+NS+TR-ThA9 Monte Carlo Simulation Study of Gas Assisted Focused Ion Beam Induced Etching, *Kyle Mahady*, *P.D. Rack*, University of Tennessee, *S. Tan*, Intel Corporation, *Y. Greenzweig*, Intel Corporation, Israel, *R.H. Livengood*, Intel Corporation, *A. Raveh*, Intel Corporation, Israel

We present a simulation study of focused ion beam etching using a gas assist. The use of a precursor gas greatly enhances material removal rate when compared to ion beam sputtering, enabling features such as valleys to be etched with lower ion doses, and consequently less damage to the substrate. The basis of our study is a Monte Carlo based code for focused ion beam milling, which simulates the cumulative removal of material due to sputtering, and secondary electron emission, for various target compositions and structures. In this talk, we describe the gas assisted etching portion of the code, which simulates monolayer adsorption of XeF<sub>2</sub> to a SiO<sub>2</sub> substrate, and the reactions between adsorbed gas and surface atoms which lead to volatilization and material removal. We study the effect of etching parameters such as beam current and gas flux on the shape of etched valleys, and the influence of ion species such as Ne<sup>+</sup> and Ga<sup>+</sup>, to characterize the underlying limitations on etching resolution. Simulations are compared against experimental results, for validation and to understand experimentally observed features.

5:20pm **HI+NS+TR-ThA10 Direct Write of Complex 3-Dimensional Structures with Helium Ion Microscopy**, *Matthew Burch*, A.V. Ievlev, Oak Ridge National Laboratory, *M.G. Stanford*, *B. Lewis*, University of Tennessee, *X. Sang*, *S. Kim*, *J. Fowlkes*, Oak Ridge National Laboratory, *P.D. Rack*, University of Tennessee, *R.R. Unocic*, *A. Belianinov*, *O.S. Ovchinnikova*, Oak Ridge National Laboratory

The next generation of computing, the generation which will follow the end of Moore's law, will need materials processing and interconnects that exist in 3-dimensions. This need has led to multiple investigations into the fabrication of complex free standing 3-dimensional structures onto any substrate at the nano-scale. Several techniques are currently being developed to fabricate free-standing micro- and nano- level structures including two-beam photon lithography and focused electron beam induced deposition (FEBID). Recent advancements in FEBID has led to the ability to simulate and subsequently fabricate complex 3D-platinum structures from an organometallic precursor.

In this work, we demonstrate the ability of the helium ion microscope (HIM) to fabricate complex 3-dimensional structures using focused ion beam deposition (FIBID) at scales smaller than previously demonstrated with FEBID. Using modern day image analytics we demonstrate a method we've successfully utilize to investigate and understand some of the most important structure-growth parameters with FIBID and how that parameter space impacts the size and morphology of created structures. These parameters include beam current, organometallic gas volume, dwell time, etc., and how these impact a grown structures length, width, and possible growth angles.

We further investigate the composition and crystalline nature utilizing scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS) in the presence of different carrier gasses of nitrogen and oxygen. We show, that in general the morphology and chemistry is nearly identical between the two gasses, that there is a slight difference in the apparent crystalline nature between the two flow gasses.

Finally, we demonstrate the minimum size structures currently grown with FIBID and the complex nature of the way these structures can be grown. We also demonstrate the HIM's unique ability to direct write structures repeatedly and reliably on non-conductive using the HIM's unique charge compensation mechanisms.

#### **Acknowledgements**

This work was conducted at the Center for Nanophase Materials Sciences, which is a Department of Energy (DOE) Office of Science User Facility.

# Thursday Evening Poster Sessions

## Tribology Focus Topic

Room: Central Hall - Session TR-ThP

## Tribology Poster Session

**TR-ThP1 Tribocorrosion Behaviour of Ti6Al4V Alloy Trated By Laser Shock Processing.** *Roman Angel Rosas Meza, G. Gómez Rosas, M. Flores Martínez, Universidad de Guadalajara, Mexico, C. Rubio González, Centro de Ingeniería y Desarrollo Industrial, Mexico, J.E. González Sevilla, Universidad de Guadalajara, Mexico*

The Ti6Al4V alloy is used in biomedical industry, currently employed in prosthesis fixing screws, there are concerns regarding its metal ion release and material loss caused by tribocorrosion in a living being. The surface functionalization by laser could improve the osseous integration of TiAl4V and reduce the damage by fretting corrosion in these screws. In this work, the laser shock processing (LSP) with two different swept densities (2500 and 5000 pulses/cm<sup>2</sup>) have been employed to know the behavior of the tribocorrosion resistance of Ti6Al4V with and without treatment. The laser used was a Nd:YAG with pulsed laser frequency of 10 Hz and wavelength of 1064 nm. The LSP configuration was the water jet mode without protective coating. The tribocorrosion tests were made with the sample immersed in a simulated body fluid containing synthetic body fluid (SBF) and bovine serum (BS) as corrosive medium, in a tribometer with reciprocating movement, using loads from 0.5 N to 1.5 N. In the tribocorrosion test was measured the evolution of open circuit potential and friction coefficient. The lost volume of the wear track was calculated using a stylus profilometer. Hole drilling test was used to measure the residual stress. The samples were characterized by means of Raman spectroscopy, scanning electron microscopy and x ray diffraction. The tribocorrosion behavior was analyzed as a function of the laser swept densities and the applied loads.

# Authors Index

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Argibay, N.: TR+AS+HI+NS+SS-WeA2, 3  
Arnott, J.: MN+BI+EM+SS+TR-TuM13, 2  
Audinot, J.-N.: HI+BI+NS+TR-ThM11, 6

## — B —

Babuska, T.F.: TR+AS+HI+NS+SS-WeA2, 3  
Belianinov, A.: HI+BI+NS+TR-ThM3, 5;  
HI+BI+NS+TR-ThM5, 5; HI+BI+NS+TR-  
ThM6, 6; HI+NS+TR-ThA10, 10  
Bernal, R.A.: TR+AS+HI+NS+SS-WeA1, 3  
Beyer, A.: HI+BI+NS+TR-ThM10, 6  
Burch, M.J.: HI+BI+NS+TR-ThM3, 5;  
HI+BI+NS+TR-ThM5, 5; HI+BI+NS+TR-  
ThM6, 6; HI+NS+TR-ThA10, 10

## — C —

Cannon, R.: HI+BI+NS+TR-ThM6, 6  
Carpick, R.W.: TR+AC+TF+VT-ThM4, 7;  
TR+AS+HI+NS+SS-WeA1, 3  
Chandross, M.: TR+AS+HI+NS+SS-WeA2, 3  
Chen, C.: MN+BI+EM+SS+TR-TuM5, 1  
Chen, P.: TR+AS+HI+NS+SS-WeA1, 3  
Cihan, E.: TR+AC+TF+VT-ThM5, 7  
Cohen, S.R.: MN+BI+EM+SS+TR-TuM12, 2  
Curry, J.F.: TR+AS+HI+NS+SS-WeA2, 3  
Curtiss, L.: TR+AS+HI+NS+SS-WeA11, 3  
Czaplewski, D.A.: MN+BI+EM+SS+TR-TuM5, 1

## — D —

Dastoor, P.C.: HI+BI+NS+TR-ThM1, 5  
De Barros Bouchet, M.-I.: TR+AC+TF+VT-ThM1,  
6  
Dienwiebel, M.: TR+AC+TF+VT-ThM5, 7  
Dowsett, D.M.F.: HI+BI+NS+TR-ThM11, 6

## — E —

Echeverrigaray, F.G.: TR+AC+TF+VT-ThM3, 7  
Egberts, P.: TR+AS+HI+NS+SS-WeA3, 3  
Ehresmann, A.: HI+BI+NS+TR-ThM10, 6  
Emmrich, D.: HI+BI+NS+TR-ThM10, 6

## — F —

Figuroa, C.A.: TR+AC+TF+VT-ThM3, 7  
Fisher, B.: TR+AS+HI+NS+SS-WeA11, 3  
Flores Martínez, M.: TR-ThP1, 11  
Fontaine, J.: TR+AC+TF+VT-ThM4, 7  
Fowlkes, J.: HI+NS+TR-ThA10, 10  
Froemel, J.: MN+BI+EM+SS+TR-TuM6, 1

## — G —

Gaul, A.: HI+BI+NS+TR-ThM10, 6  
Gözlhäuser, A.: HI+BI+NS+TR-ThM10, 6  
Gómez Rosas, G.: TR-ThP1, 11  
Gong, P.: TR+AS+HI+NS+SS-WeA3, 3  
González Sevilla, J.E.: TR-ThP1, 11  
Greenzweig, Y.: HI+NS+TR-ThA9, 9

## — H —

Halsted, M.: HI+BI+NS+TR-ThM3, 5  
Harrison, J.A.: TR+AS+HI+NS+SS-WeA1, 3  
Hart, S.M.: TR+AC+TF+VT-ThM12, 7  
Herrmann, C.: HI+BI+NS+TR-ThM4, 5  
Hilbert, J.: TR+AC+TF+VT-ThM4, 7  
Hla, S.W.: TR+AS+HI+NS+SS-WeA11, 3

Holzinger, D.: HI+BI+NS+TR-ThM10, 6  
Hormel, T.T.: TR+AC+TF+VT-ThM12, 7  
Hysmith, H.: HI+BI+NS+TR-ThM5, 5

## — I —

Ievlev, A.V.: HI+BI+NS+TR-ThM5, 5;  
HI+NS+TR-ThA10, 10

## — J —

Jeng, Y.-R.: TR+AS+HI+NS+SS-WeA1, 3  
Jesse, S.: HI+BI+NS+TR-ThM6, 6

## — K —

Kanzaki, T.: HI+NS+TR-ThA6, 9  
Karimian, F.: HI+BI+NS+TR-ThM10, 6  
Kavanagh, K.: HI+BI+NS+TR-ThM4, 5  
Keimel, C.: MN+BI+EM+SS+TR-TuM1, 1  
Khadka, S.: TR+AS+HI+NS+SS-WeA11, 3  
Kim, S.: HI+BI+NS+TR-ThM3, 5;  
HI+BI+NS+TR-ThM6, 6; HI+NS+TR-ThA10,  
10

Klug, M.: HI+BI+NS+TR-ThM10, 6  
Koshigan, M.: TR+AC+TF+VT-ThM4, 7  
Krick, B.A.: TR+AS+HI+NS+SS-WeA2, 3

## — L —

Lagally, M.: HI+BI+NS+TR-ThM4, 5  
Lamb, R.N.: MN+BI+EM+SS+TR-TuM13, 2  
Levings, P.P.: TR+AC+TF+VT-ThM12, 7  
Lewis, B.: HI+NS+TR-ThA10, 10  
Li, Y.: TR+AS+HI+NS+SS-WeA11, 3  
Lieber, C.M.: TR+AS+HI+NS+SS-WeA9, 3  
Livengood, R.H.: HI+NS+TR-ThA9, 9  
Lopez, D.: MN+BI+EM+SS+TR-TuM5, 1  
Lubomirsky, I.: MN+BI+EM+SS+TR-TuM12, 2  
Luftman, H.: TR+AS+HI+NS+SS-WeA2, 3  
Luo, L.: HI+BI+NS+TR-ThM5, 5

## — M —

Madiona, R.M.T.: HI+NS+TR-ThA3, 9  
Mahady, K.: HI+BI+NS+TR-ThM5, 5;  
HI+NS+TR-ThA9, 9  
Makagon, E.: MN+BI+EM+SS+TR-TuM12, 2  
Mangolini, F.: TR+AC+TF+VT-ThM4, 7  
Marks, L.: TR+AC+TF+VT-ThM10, 7  
Marshall, S.L.: TR+AC+TF+VT-ThM12, 7  
McClimon, J.B.: TR+AC+TF+VT-ThM4, 7  
McCord, J.: HI+BI+NS+TR-ThM10, 6  
Michels, A.F.: TR+AC+TF+VT-ThM3, 7  
Miline, Z.: TR+AS+HI+NS+SS-WeA1, 3  
Mishuk, E.: MN+BI+EM+SS+TR-TuM12, 2  
Mizuta, H.: HI+NS+TR-ThA6, 9  
Muir, B.W.: HI+NS+TR-ThA3, 9  
Muruganathan, M.: HI+NS+TR-ThA6, 9

## — N —

Narayanan, B.: TR+AS+HI+NS+SS-WeA11, 3  
Ngo, A.: TR+AS+HI+NS+SS-WeA11, 3  
Nguyen, M.P.: MN+BI+EM+SS+TR-TuM6, 1  
Notte, J.A.: HI+BI+NS+TR-ThM11, 6

## — O —

O'Bryan, C.S.: TR+AC+TF+VT-ThM12, 7  
Ogawa, S.: HI+NS+TR-ThA6, 9  
Ohlhausen, J.A.: TR+AC+TF+VT-ThM4, 7  
Ovchinnikova, O.S.: HI+BI+NS+TR-ThM5, 5;  
HI+NS+TR-ThA10, 10

Ovchinnikova, O.S.: HI+BI+NS+TR-ThM6, 6;  
HI+NS+TR-ThA1, 9

## — P —

Pigram, P.J.: HI+NS+TR-ThA3, 9  
Pitenis, A.A.: TR+AC+TF+VT-ThM12, 7  
Popovitz-Biro, R.: MN+BI+EM+SS+TR-TuM12,  
2

## — R —

Rack, P.D.: HI+BI+NS+TR-ThM5, 5; HI+NS+TR-  
ThA10, 10; HI+NS+TR-ThA9, 9  
Raveh, A.: HI+NS+TR-ThA9, 9  
Rechav, K.: MN+BI+EM+SS+TR-TuM12, 2  
Retterer, S.: HI+BI+NS+TR-ThM3, 5  
Righi, M.C.: TR+AS+HI+NS+SS-WeA7, 3  
Rosas Meza, R.A.: TR-ThP1, 11  
Rosenhahn, A.: MN+BI+EM+SS+TR-TuM13, 2  
Rubio González, C.: TR-ThP1, 11

## — S —

Sales de Mello, S.R.: TR+AC+TF+VT-ThM3, 7  
Sang, X.: HI+NS+TR-ThA10, 10  
Sankaranarayanan, S.: TR+AS+HI+NS+SS-  
WeA11, 3  
Sawyer, W.G.: TR+AC+TF+VT-ThM12, 7  
Schall, J.D.: TR+AS+HI+NS+SS-WeA1, 3  
Schmidt, M.E.: HI+NS+TR-ThA6, 9  
Schulze, K.D.: TR+AC+TF+VT-ThM12, 7  
Scoble, J.A.: HI+NS+TR-ThA3, 9  
Scott, S.A.: HI+BI+NS+TR-ThM4, 5  
Seal, S.: MN+BI+EM+SS+TR-TuM10, 2  
Shaw, S.W.: MN+BI+EM+SS+TR-TuM5, 1  
Sheehan, P.E.: TR+AS+HI+NS+SS-WeA9, 3  
Simovich, T.: MN+BI+EM+SS+TR-TuM13, 2  
Stanford, M.G.: HI+NS+TR-ThA10, 10  
Strandwitz, N.C.: TR+AS+HI+NS+SS-WeA2, 3

## — T —

Tan, S.: HI+NS+TR-ThA9, 9  
Tanaka, S.: MN+BI+EM+SS+TR-TuM6, 1  
Tsai, P.: TR+AS+HI+NS+SS-WeA1, 3  
Turner, K.T.: TR+AS+HI+NS+SS-WeA1, 3

## — U —

Unocic, R.R.: HI+NS+TR-ThA10, 10  
Urueña, J.M.: TR+AC+TF+VT-ThM12, 7

## — V —

Van Benthem, M.H.: TR+AC+TF+VT-ThM4, 7  
Vollnhals, F.: HI+BI+NS+TR-ThM11, 6

## — W —

Wachtel, E.: MN+BI+EM+SS+TR-TuM12, 2  
Weinstein, D.: MN+BI+EM+SS+TR-TuM3, 1  
Welch, N.G.: HI+NS+TR-ThA3, 9  
Wilson, M.: TR+AS+HI+NS+SS-WeA2, 3  
Wirtz, T.: HI+BI+NS+TR-ThM11, 6

## — Y —

Yakovlev, S.: HI+BI+NS+TR-ThM5, 5  
Ye, Z.: TR+AS+HI+NS+SS-WeA3, 3  
Yuan, L.: TR+AS+HI+NS+SS-WeA3, 3

## — Z —

Zanette, D.H.: MN+BI+EM+SS+TR-TuM5, 1  
Zhang, Y.: TR+AS+HI+NS+SS-WeA11, 3