

Thursday Morning, October 18, 2007

Tribology

Room: 617 - Session TR2+BI+NS+MN-ThM

Biolubrication, Sensing and Adhesion

Moderator: R.W. Carpick, University of Pennsylvania

8:00am **TR2+BI+NS+MN-ThM1 Resonant Nanomechanical Sensors for Protein Detection**, *P.S. Waggoner, H.G. Craighead*, Cornell University

Micro- and nanoelectromechanical systems (MEMS and NEMS) are of interest in sensing applications due to their high sensitivity, label-free operation, and potential for multiplexed detection on a single chip. Resonant MEMS and NEMS devices have demonstrated detection of masses on the order of femtograms or less, transducing changes in mass into changes in resonant frequency. Appropriate functionalization of the sensor surface allows specific, label free detection for analytes of choice. In this work we have detected prostate specific antigen (PSA), a biomarker used in the early detection of prostate cancer, as a model system using immunospecific functional layers present on the resonator surfaces. We have also studied the surface chemistry in order to minimize non-specific binding during sensor functionalization and use. In addition, sandwich assay techniques have been investigated for use in secondary mass tagging in order to enhance sensor response for dilute analytes while still preserving specificity.

8:20am **TR2+BI+NS+MN-ThM2 Correlation between XPS Data and Liquid Phase Self-Assembly of Alkanethiols**, *H.M. Meyer III, T.G. Thundat, R. Desikan*, Oak Ridge National Laboratory, *R.G. White*, Thermo Fisher Scientific, UK

The relative ease in which self-assembled monolayers (SAM) can be applied have made them part of the standard tool set used for functionalizing and patterning surfaces at the nanoscale. Recently, alkanethiol-based SAMs have been used for immobilizing selective chemical receptors on the gold-coated side of a microcantilever. In this configuration, adsorption on the functionalized side of the microcantilever generates nanomechanical motion (i.e. bending) which can be accurately sensed and used for detecting a variety of chemical and biological molecules. Achieving reliable selectivity and sensitivity depends primarily on the reproducible formation of the functional layer on one side of the microcantilever. We have recently investigated the effect of chain length on the packing density of the alkanethiols and, in turn, how this affects the sensitivity of the sensor. We present XPS characterization of microfabricated cantilevers functionalized with alkanethiol-based SAMs. The results are correlated with similar cantilevers that have been monitored during adsorption/immobilization of the same alkanethiols in the liquid phase. Previous liquid phase results indicated an unusual change in packing density of the thiol molecules as the chain length was increased and were difficult to correlate with preliminary XPS data, indicating major difference between how these films form in liquid phase vs. post-formation analysis in-vacuo. These new results attempt to illuminate those differences. Research sponsored in part by grant NSF Award ID 0330410 in collaboration with Drs. V.P. Dravid, G. Shekhawat, and A. Majumdar and in part by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of FreedomCAR and Vehicle Technologies, as part of the High Temperature Materials Laboratory User Program, Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U.S. Department of Energy under contract number DE-AC05-00OR22725.

8:40am **TR2+BI+NS+MN-ThM3 Surface-Chemical Aspects of Implant Biotribology and Biomimetic Lubrication**, *N.D. Spencer*, ETH Zurich, Switzerland

INVITED

Following implantation of a hip prosthesis, the synovial membrane reforms and generates a liquid, pseudo synovial fluid (PSF), which is comparable in composition to synovial fluid itself. This complex solution of proteins, glycoproteins, polysaccharides and lipids is then responsible for the lubrication of the implanted joint. Surprisingly, the interactions of PSF components with the surfaces of joint materials, such as UHMWPE, CoCrMo, or alumina, remain remarkably unexplored. Not only is their relative propensity for adsorption unknown, but, once adsorbed, their efficacy for lubrication remains to be determined. We have investigated these issues by means of tribometry (on both macro and nano scales), combined with fluorescence microscopy, and determined, for example, that while albumin, the major component of PSF and the model protein used for

implant testing, is strongly adsorbed on the surface of implants, it can be displaced during sliding by $\hat{I}\pm$ -glycoprotein, a species present at much lower concentrations, but a much more effective lubricant. The fluorescence approach has also enabled us to detect transfer of polyethylene under conditions where it was not previously thought to occur. Natural lubricated surfaces tend to be soft and covered with species such as polysaccharides that have the ability to retain large amounts of water. We have attempted to imitate and understand this mechanism of lubrication by means of tethering various highly hydrated polymer chains in a brush-like structure onto both hard and soft surfaces and measuring their tribological properties. Interestingly, on soft surfaces, the effect of chain tethering seems to be to effectively eliminate boundary lubrication entirely. Fluid-film-like behavior is thought to persist to very low sliding speeds, by virtue of water retention in a thin layer between the brush-covered surfaces.

9:20am **TR2+BI+NS+MN-ThM5 In-situ Measurement of Boundary-Lubrication on Articular Cartilage Surfaces**, *J.M. Coles*, Duke University, *G.D. Jay*, Brown University, *F. Guilak*, *S. Zauscher*, Duke University

The diarthrodial (synovial) joints of the body enable locomotion and activity while withstanding millions of cycles of loading at several times body weight. Recent macroscopic tribological experiments and biochemical analyses suggest that heavily glycosylated proteoglycans encoded by the gene proteoglycan 4 (Prg4), which are expressed by synoviocytes in synovial fluid as lubricin and by superficial zone chondrocytes of articular cartilage as surface zone protein (SZP), provide boundary lubrication in cartilage in the absence of interstitial fluid pressurization. Improved understanding of the role of Prg4 on the cartilage surface could thus provide important insight into the development of new therapies for joint diseases such as OA. The development of powerful new methods for the genetic manipulation of mice has led to the creation of modified murine strains in which specific gene inactivation (PRG4^{-/-}) results in age-related joint degeneration that recapitulates the symptoms of OA. Here we show that atomic force microscopy with a colloidal probe is uniquely suited to study boundary lubrication of murine cartilage in-situ and in absence of other lubrication mechanisms. Here we report on friction measurements on the superficial surface layer of articular cartilage from the femoral head of Prg4 knockout and wildtype mice under boundary lubrication conditions. Furthermore, we report on the measured RMS roughness and Young's modulus to quantify morphological and mechanical changes of the cartilage superficial zone induced by the absence of Prg4. Our measurements suggest that the absence of Prg4 leads to increased friction, as well as degradation of the mechanical and topographical properties of cartilage. We propose that, while lubricin plays a role as a boundary lubricant, its role in chondroprotection is equally, if not more, vital.

9:40am **TR2+BI+NS+MN-ThM6 Humidity Dependent Ordering of Water and its Effect on Adhesion and Friction between Silica Surfaces**, *B.I. Kim*, *J. Bonander*, Boise State University

Adhesion and friction related to water are major problems limiting both the fabrication and long-term use of micro-machines. Adhesion and friction between two silica surfaces were measured as a function of separation distance using interfacial force microscope (IFM) for different relative humidity (RH) between 3% - 78%. The IFM provides force-distance curves without having the "snap-to-contact" problems associated with atomic force microscopy using voltage-controlled force feedback. The measured friction force-distance curves show that the friction force is oscillatory as the separation changes below thickness of water droplet. The oscillatory period is close to the mean diameter of a water molecule. The number of oscillation increased as the relative humidity increases up to RH 60% while it decreased with humidity above RH 60%. The origin of the oscillatory feature in the "interfacial" water may come from the "solid-liquid transition" between solid (ordering) and liquid (disordering). Strong correlation between the number of oscillation and the strength of the adhesion and friction indicates that the humidity dependent adhesion and friction may be attributed to the ordered structure of water molecules between two silica surfaces.

10:00am **TR2+BI+NS+MN-ThM7 Nanomechanical Properties of Arachidic Acid Langmuir Blodgett Films**, *G. Oncins*, University of Barcelona, Spain, *J. Torrent-Burgues*, Universitat Politècnica de Catalunya, Spain, *F. Sanz*, Universitat de Barcelona and Center of Nanobioengineering of Catalonia (IBEC), Spain

Scanning Probe Microscopies development has given biophysics the possibility to deal with the interactions arisen in biological membranes from a nanometric point of view, revealing that van der Waals, hydrogen bonding and electrostatic interactions play a crucial role in the membrane

cohesion. Unfortunately, although interesting experimental conclusions have been reported in the past, these systems are complex and difficult to study.¹ In order to isolate the effect of the different cohesive interactions, Langmuir-Blodgett (LB) fatty acid monolayers provide excellent model systems because of the controlled area per molecule, linear hydrocarbon chain geometry, amphiphilic nature, high mechanical stability and the possibility to test solid and liquid phases at room temperature. The nanomechanical properties of arachidic acid LB films extracted at surface pressures of 1, 15 and 35 mN/m and deposited on mica are investigated by Atomic Force Microscopy, Force Spectroscopy and Friction Force Microscopy. It is experimentally demonstrated that the molecular ordering depends on the extraction pressure, while discrete molecular tilting angles of 50°, 34° and 22° are detected and identified as conformations that maximize van der Waals interactions between alkyl chains. The vertical force (F_v) needed to puncture the monolayer strongly depends on the molecular tilting angle, ranging from 13.07±3.24 nN at 1 mN/m to 22.94±5.49 nN at 35 mN/m. The friction force (F_f) measurements performed from low F_v until monolayer disruption reveal three friction regimes corresponding with a low F_f elastic monolayer deformation at low F_v , followed by a sharp increase in F_f due to a sudden plastic deformation of the monolayer. The last regime corresponds with the monolayer rupture and the contact between tip and substrate. Interestingly, as the extraction pressure increases, the friction coefficient of the monolayer reduces while the F_v needed to trigger the monolayer plastic deformation increases, facts that are discussed in terms of sample compactness and monolayer rupture mechanism.²

¹ Garcia-Manyes, S.; Oncins, G.; Sanz, F. *Biophys. J.* 2005, 89, 1812.

² Oncins, G.; Garcia-Manyes, S.; Sanz, F. *Langmuir* 2005, 21, 7373.

10:20am **TR2+BI+NS+MN-ThM8 Optimal Roughness for Minimal Adhesion**, *D.L. Liu*, Worcester Polytechnic Institute, *J. Martin*, Analog Devices Inc., *N.A. Burnham*, Worcester Polytechnic Institute

Differing views on the effect of surface roughness on adhesion have appeared in the literature recently. Molecular dynamics has been used to simulate the contact of two surfaces and found that atomic-scale roughness can have a large influence on adhesion, causing the breakdown of continuum mechanics models.¹ An experimental study showed that roughness can determine the adhesion in nanometer contacts and indicated that continuum mechanics still works down to nanometer length scales.² In this work, we use a single-asperity model to describe a smooth tip in contact with a rough surface and predict that there is an optimal size of asperity that will yield a minimum of adhesion. Experimentally, adhesive forces on silicon wafers with varying roughness from 0.2 nm to 39 nm were measured using AFM (atomic force microscope) cantilevers with varying tip radii ranging from 75 nm to 9.08 μ m. It is found that for all tip radii, the adhesion falls significantly for roughness greater than 1-2 nm and drops at higher roughness for larger tips. Minimum adhesion was observed as predicted in the 1-10 nm range and the optimal roughness for minimal adhesion increases as the tip radius increases, which is also consistent with our predictions. The work presented here should help minimize adhesion in future MEMS devices and progress the understanding of adhesion between the atomic- and macro-scale.

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

² E.J. Thoreson, J. Martin, N.A. Burnham, *J. Colloid Interface Sci.* 298, 94-101 (2006).

10:40am **TR2+BI+NS+MN-ThM9 A Tribological Study of Bound plus Mobile Lubricants for MEMS Application from the Nano- to the Macro-scale Regime**, *B.P. Miller*, *M. Brukman*, North Carolina State University, *C.C. Baker*, Naval Research Laboratory, *R.J. Nemanich*, North Carolina State University, *K.J. Wahl*, Naval Research Laboratory, *J. Krim*, North Carolina State University

One possible solution to the in-use stiction problem in Micro-Electro-Mechanical systems (MEMS) is the introduction of a bound plus mobile lubricant combination.¹ For this system, one monolayer of the bound lubricant (perfluorodecyltrichlorosilane, PFTS) bonds to the surface of the device. The mobile lubricant (tricresyl phosphate, TCP) can replenish the layer after rubbing contacts wear it away, thus keeping the device free of contamination. Friction behavior of this lubricant combination was examined over three different regimes using a macroscopic tribometer, an AFM, and a quartz crystal microbalance (QCM). A comparative study of bound only versus bound plus mobile lubricants showed a decrease of the coefficient of friction with the addition of the mobile lubricant to the bound layer. Dynamic properties of the mobile film were characterized with the QCM. This work is funded by AFOSR Extreme Friction MURI Grant #FA9550-04-1-0381.

¹W. Neeyakorn, M. Varma, C. Jaye, J. E. Burnette, S.M. Lee, R. J. Nemanich, C. Grant, J. Krim, Dynamics of Vapor-Phase Organophosphates on Silicon and OTS, *Tribology Letters*, in press.

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