

Wednesday Afternoon, October 30, 2013

Thin Film

Room: 104 A - Session TF+AS+BI+EM+SE+SS-WeA

Applications of Self-Assembled Monolayers and Nano-Structured Assemblies

Moderator: M.R. Linford, Brigham Young University, H. Zuilhof, Wageningen University, Netherlands

2:00pm **TF+AS+BI+EM+SE+SS-WeA1 Enhanced Multiphoton Processes for Molecule Localization on Plasmonic Nanostructures, J. Shumaker-Parry**, University of Utah **INVITED**

Plasmonic nanostructures produce enhanced optical near fields as a result of localized surface plasmon resonances (LSPRs). Tailoring of the nanostructure size, shape, and inter-structure spacing provides tuning of the LSPR properties including the near field behavior. We use two approaches to produce plasmonic architectures with enhanced fields. First, we have developed an asymmetric functionalization process to create nanoparticle assemblies by controlling the localization of molecules on the surface of the nanoparticles. The spatial localization of the molecules on the Janus-like particles lead to controlled assembly and direction of molecules into regions of enhanced near fields, a process that can be monitored through enhanced spectroscopy. The second approach we use is based on nanosphere template lithography to fabricate uniquely-shaped plasmonic nanoantennas. One example is the nanocrescent which exhibits polarization dependent LSPR responses across a broad spectral range, from the visible through the mid-infrared regions. Simulations of the LSPR response predict localized, inhomogeneous near fields around the nanocrescent antennas. We mapped the local fields of nanocrescents through an enhanced multiphoton photopolymerization process. Local cross-linking of a photopolymer provides evidence of the near field behavior and confirms the predicted polarization-dependent enhanced fields. Localized photopolymerization can be used to spatially localize molecules at the nanoscale through these enhanced fields created by the plasmonic nanoantennas.

2:40pm **TF+AS+BI+EM+SE+SS-WeA3 A Path towards Single-Electron Devices, P. Campbell**, University of Texas at Dallas, *L. Caillard, O. Pluchery*, University of Pierre and Marie Curie, France, *Y.J. Chabal*, University of Texas at Dallas

As the minimum feature size in CMOS technology continues to decrease, quantum effects begin to dominate the operation of the transistors. In order to compensate for these effects, we require a new transistor design that operates based on the quantum effects present at the nanoscale. Single-electron transistors present a viable option to create smaller, more efficient transistors but a high-yield process has not yet been developed for their manufacturing.

In addition to the increasing effect of quantum mechanics, current lithographic methods face challenges in scaling below the 10 - 20 nm scale. Several proposed lithographic methods, such as direct write methods, can provide high resolution lithography, enabling the creation of transistors in the sub-10 nm region. However, direct write methods require extensive development of multi-tip approaches to achieve throughput comparable to optical lithography.

A chemical method to fabricate devices can create high performance transistors with a high throughput. The first step of this process is the deposition of a monolayer of organic molecules on a hydrogen-passivated silicon surface. Second, mono-dispersed gold nanoparticles are deposited on the surface to form a tunnel junction. The electrical properties of the sample are determined by probing the surface with scanning tunneling microscopy (STM). This results in a double-tunnel junction. By properly tailoring the nanoparticle size, organic molecule size, and STM tip-sample distance, a Coulomb staircase can be observed in the I-V curve of the junction [1].

Using a 1.7 nm thick organic molecule, evidence consistent with a Coulomb staircase is observable on a small number of spectroscopy curves. However, the electronic response of each nanoparticle is not consistent. This suggests that thermal and electronic noise play a significant role in the measurement and behavior of double-tunnel junctions. As well, the properties of the junction are influenced greatly by the quality of the interface between the substrate and organic layer and the organic layer itself. By exploring the chemistry of varying length molecules on the surface and characterizing the quality of attachment and durability of the organic layer, optimization of the samples is possible to create more reliable double tunnel junctions.

References:

[1] K. Mullen, E. Enjacob, R.C. Jaklevic, Z. Schuss. I-V Characteristics of Coupled Ultrasmall-Capacitance Normal Tunnel-Junctions. *Phys. Rev. B* 37 (1988) 98-105.

3:20pm **TF+AS+BI+EM+SE+SS-WeA5 Chemical and Electronic Interface Formation between a Monolayer and Cobalt, S. Pookpanratana, H.-J. Jang, L.K. Lydecker, C.A. Richter, C.A. Hacker**, National Institute of Standards and Technology (NIST)

Organic-based electronics are attractive for next-generation applications because of the wide range of possibilities in tailoring the chemical structure of molecules for a desired functionality. An emerging field is to combine the flexibility of organic materials into spintronics. While the self-assembly of molecular layers onto Au is well-studied, self-assembly does not form as readily between molecules and a ferromagnetic metal due to the lack of control of the interface composition (i. e., oxide formation). Conventional approaches to fabricate hybrid organic-metal interfaces have relied on vacuum-based physical vapor deposited organic molecules since the metal-organic interface can be better controlled. However, vacuum-based deposition of organic materials limits the manufacturing and applications of such hybrid systems making solution-based processes attractive for organic-based electronics. We have explored self-assembled monolayers (SAM) on a template-stripped Co surface to understand the molecular-metal interface from a structural, chemical, and electronic point of view.

Template-stripped Co is a method to prepare consistent surfaces that can be used in ambient conditions. First, Co is evaporated onto a molecular layer-treated Si (tSi) surface, and then the Co surface is laminated to a plastic substrate. The plastic/Co surface is stripped off of the tSi and immediately placed into SAM solution. We chose octadecanethiol (ODT) and mercaptohexadecanoic acid (MHA) as “fruit fly” molecules to self-assemble onto Co. This hybrid molecule-metal interface is investigated by using microscopy, infrared spectroscopy, and photoelectron spectroscopy to provide details of the physical, chemical, and electronic structure at that interface.

The self-assembly of ODT and MHA are directly confirmed by infrared spectroscopy and X-ray photoelectron spectroscopy (XPS). The absorbance intensities of the C-H stretches of ODT and MHA on Co are comparable to those on Au, which indicates similar packing density on both surfaces. MHA has the added complexity with both the -SH and -COOH functional groups are able to bond. Moreover, the -COOH groups also affect the Co surface by reducing the native oxide as shown by XPS. Molecular electronic junctions formed on Si by flip-chip lamination [1] show that electron transport is heavily influenced by the MHA/Co interface or Co electrode when compared to a Si/MHA/Au control device. Preliminary results suggest that SAMs on Co surfaces are a promising route for controlling the organic-ferromagnet interface for next generation devices.

[1] M. Coll et al., *J. Am. Chem. Soc.* 2009, 131, 12451-12457.

4:00pm **TF+AS+BI+EM+SE+SS-WeA7 Stability of the Molecule-Substrate Interface in SAMs Probed by SIMS – Experiments and Simulations, J.W. Ossowski, J. Rysz, D. Maciazek**, Jagiellonian University, Poland, *M. Krawiec*, Maria Curie-Skłodowska University, Poland, *Z. Postawa*, Jagiellonian University, Poland, *A. Terfort*, Goethe University, Germany, *P. Cyganik*, Jagiellonian University, Poland

Self-Assembled Monolayers (SAMs) play nowadays a key role in many aspects of nanotechnology ranging from patterning and molecular electronics up to biocompatible materials. One of the key requirements for successful use of SAMs in all of these applications is a control of their stability at the molecule-substrate interface. Analysis of this interface is however extremely difficult for technologically relevant, and therefore, more complicated SAMs. In this presentation we report extensive static secondary ion mass spectrometry (SIMS) studies on series of thiols and selenols on Au(111) substrates where structure and stability of molecule-substrate interface were systematically modified.¹ Correlating SIMS data with our previous microscopic^{2,3}, spectroscopic⁴ and neutral mass spectrometry studies^{5,6} we show that, SIMS can be successfully applied to monitor fine changes in the molecule-substrate interface stability of these model SAMs. To reveal the possible mechanism of ion-induced desorption sensitivity to the SAM-substrate interface energetics we discuss also results of our molecular-dynamic (MD) simulations of the desorption process for this system with starting structure calculated by DFT calculations.¹ Our data show that a new approach for probing the stability of molecule-substrate interface in SAMs can be proposed by using such relatively popular and fast technique as SIMS, which can be applied for virtually all complicated and technologically relevant SAMs.

References

- (1) J. Ossowski, P. J. Rysz, D. Maciazek, M. Krawiec, Z. Postawa, A. Terfort and P. Cyganik *submitted*.
- (2) P. Cyganik, K. Szlagowska-Kunstman, et al. *J. Phys. Chem. C* **2008**, *112*, 15466.
- (3) M. Dendzik, A. Terfort, P. Cyganik *J. Phys. Chem. C* **2012**, *116*, 19535.
- (4) K. Szlagowska-Kunstman, P. Cyganik, et al. *Phys. Chem. Chem. Phys.* **2010**, *12*, 4400.
- (5) S. Wyczawska, P. Cyganik, A. Terfort, P. Lievens, *ChemPhysChem(Communication)* **2011**, *12*, 2554.
- (6) F. Vervaecke, S. Wyczawska, P. Cyganik, et al. *ChemPhysChem(Communication)* **2011**, *12*, 140.

4:20pm TF+AS+BI+EM+SE+SS-WeA8 Controlled Modification of Protein-Repelling Monomolecular Films by Ultraviolet Light: The Effect of Wavelength and Implications for Lithography. *Y.L. Jeyachandran*, University of Heidelberg, Germany, *A. Terfort*, Frankfurt University, Germany, *M. Zharnikov*, University of Heidelberg, Germany

Advanced lithographic techniques applied to monomolecular resists enable the fabrication of well-defined patterns of functional biomolecules, above all proteins, and specific receptors, which are the key elements of biosensors, bio-fouling analysis assays, cell studies, and tissue engineering applications. An essential element of such patterns is a protein-repelling "background" surrounding the pre-selected sensing areas and preventing non-specific adsorption of proteins beyond these regions. Here we use protein-repelling oligo(ethylene glycol) (OEG) terminated alkanethiolate (AT) monolayers on gold as matrix for the preparation of such patterns. Exposure of this matrix to ultraviolet (UV) light results in the damage of the OEG chains and photooxidation of the thiolate headgroups, which can be used for controlled tuning of protein-repelling properties within so-called UV direct writing (UVDW) approach or for the preparation of mixed OEG-AT/specific-receptor films by so-called UV-promoted exchange reaction (UUPER). Using several model systems, we studied the effect of the wavelength (254 – 390 nm) on the course and efficiency of the UVDW and UUPER processes applied to different OEG-AT matrices. The cross sections of the UV induced damage were found to decrease significantly with increasing wavelength of UV light. In accordance with this behavior, the efficiencies of both UVDW and UUPER were maximal at a wavelength of 254 nm, somewhat lower at 313 and 365 nm, and lowest at 390 nm. Both UVDW and UUPER allowed a fine tuning of protein affinity for non-specific and specific adsorption, respectively, but UVDW did not occur below a certain, wavelength-dependent threshold dose. Performing UUPER below this dose enables to suppress possible non-specific adsorption of proteins even in the case of non-complete exchange of the UV-damaged molecules of the primary OEG-AT matrix by receptor-bearing moieties. The obtained results are of direct relevance for the preparation of high-quality mixed OEG-AT/specific-receptor films and the fabrication of complex protein patterns.

4:40pm TF+AS+BI+EM+SE+SS-WeA9 The 2D Self-Assembly of Strongly Dipolar Molecules. *A. Enders*, *D. Kunkel*, *S. Beniwal*, *P.A. Dowben*, University of Nebraska Lincoln, *S. Simpson*, *E. Zurek*, State University of New York at Buffalo

The self-assembly of organic molecules on flat metal surfaces can differ considerably from the well-known solution-based supramolecular chemistry. Substrates may set limits to the mobility of molecular adsorbates, and interactions across the organic/inorganic interface may perturb the electronic structure of the molecules and the substrate considerably. As a result, their diffusivity, the strength of chemical bonds, charge, protonation and deprotonation may all be dependent on the substrate itself. This can be exploited to engineer unique structures and properties that may not exist naturally in the respective crystalline phase.

One of the central questions in organic self-assembly is the role of an intrinsic molecular electric dipole and how the resulting electrostatic interaction competes with other chemical bonds. We studied small molecules with large intrinsic electrical dipole as model system for molecular films adsorption on surfaces for altering the interface dipole screening. For instance, we investigated the self-assembly and interface properties of zwitterionic molecules of type C6H2(...NHR)2(...O)2 (R = H, ...), adsorbed on Cu(111), Ag(111), Au(111) surfaces with scanning tunneling microscopy in UHV [1]. These molecules carry positive and negative charges on opposite parts of the molecule, resulting in a huge electric dipole of typically 10 Debye. We find that the dipole of the surface-supported molecule is decreased with respect to free species and of order of 1 - 2 Debye, depending on the substrate material. The molecules self-assemble into 2D structures upon adsorption, where the substrate-dependent strength of the dipolar interactions between the adsorbed molecules can dictate the network architecture. DFT calculations were performed to analyze adsorption geometry, charge transfer and dipole moment. By

systematic comparison of the self-assembly of those molecules on different metal substrates we were able to show that the intrinsic dipole mainly plays a role in the structure formation if the interaction strength with the substrate is very weak, otherwise epitaxial fit to the substrate dictates the molecular arrangement.

5:00pm TF+AS+BI+EM+SE+SS-WeA10 Quasicrystalline Ordering in Small-Molecule Self-Assembly. *N.A. Wasio*, *R.C. Quardokus*, *R.P. Forrest*, *C.S. Lent*, *S.A. Corcelli*, *J.A. Christie*, *K.W. Henderson*, *S.A. Kandel*, University of Notre Dame

Scanning tunneling microscopy was used to study self-assembly of carboxylic acid monolayers. In most cases, the formation of two strong hydrogen bonds results in dimer formation; in some others, linear catemer chains are formed. We report the observation of a five-membered catemer ring, stabilized by additional CH...O interactions available in the cyclic structure. We confirm the existence of CH...O hydrogen bonding, both with density functional theory calculations and by observing the disappearance of pentamers when molecules without suitable CH donors are used. Long-range assembly of pentamers results in a two-dimensional quasicrystalline lattice, the first observation of such structure from small-molecule self-assembly.

5:20pm TF+AS+BI+EM+SE+SS-WeA11 Unexpected Behaviour of Liquid Wetting at the Limit of Small-Scale Surface Topography. *J. Knauf*, Advanced Molecular Films GmbH and RWTH Aachen University, Germany, *L. Reddemann*, Advanced Molecular Films GmbH and Universität zu Köln, Germany, *A. Böker*, RWTH Aachen University and DWI an der RWTH Aachen e.V., Germany, *K. Reihls*, Advanced Molecular Films GmbH, Germany

The size of topographic surface structures that affect wetting can be as small as sub-nanometer dimensions. As a model system we prepare monolayer from binary mixtures of 1H,1H,2H,2H-perfluoroalkyl thiols of different chain lengths on gold. Detailed characterization by static secondary ion mass spectrometry and ellipsometry confirm binary monolayer of randomly mixed constituents. Owing to their stiff helical conformation such perfluoroalkyl chains create topographic features of well-characterized sub-nanometer dimensions. As a result, surface topographies of randomly distributed long and short chains of a height difference of 1.2 Å per CF₂ group and a next neighbor distance of 5.8 Å are obtained.

We present comprehensive investigations of wetting properties of such binary monolayers of various molar fractions and chain length differences. As an example, a binary mixed monolayer from 1H,1H,2H,2H-perfluorodecyl and 1H,1H,2H,2H-perfluorododecyl thiols, thus differing by two CF₂ groups increase the advancing water contact angle from 116.0° for either one of the single component monolayer by about 2° to 117.7° for a surface of an equimolar composition of the two constituents. Such increase is considerably less than expected from simple thermodynamic models. Wenzel's equation of wetting on rough surfaces predicts an advancing angle difference of 7°. Results of contact angles of different liquids on various sub-nanometer size topographies will be presented and discussed assuming an apparent effective reduction of surface energy at short length scales similar to results obtained from grazing-incidence X-ray scattering experiments [1].

[1] S. Mora *et al.*, *Phys. Rev. Lett.* **90**, 216101 (2003)

5:40pm TF+AS+BI+EM+SE+SS-WeA12 The Balance between Transparency and Roughness on a Superhydrophobic Coating. *C. Wang*, *A. Wu*, *R. Lamb*, University of Melbourne, Australia

High orders of interfacial roughness are known to scatter light; as a result, superhydrophobic surfaces, which are inherently rough, generally appear opaque. Therefore, an ideal range of roughness that can provide both superhydrophobicity and low light scattering in the visible light spectrum is a highly attractive challenge. The use of self-assembling nanoparticles is a popular choice to generate the required roughness for superhydrophobicity. While such systems offer ease of fabrication and processing, coating thickness is generally kept to a minimum to reduce light scattering, below the light scattering threshold, typically in the sub-micron scale. The degree of roughness in a sol-gel synthesized coating can be manipulated using differences in solvent polarity and vapor pressures. There is a clear trend in solvent-particle and particle-particle interaction under polar and non-polar solvents, resulting in a difference in nanoparticle cluster size^[1], which contributes to light scattering. Changes in vapor pressure can also result in surface morphology formation during the drying process. We demonstrate that a simple change in solvent polarity on a sol-gel system can increase the optical transparency of a coating of thickness > 1 µm from 82-96% to 93-100% transparent in the visible spectrum. Meanwhile, the increased drying temperature from 100°C to 350°C can transform the coating's hydrophobicity to superhydrophobicity.

1. Khan, S.A. and N.J. Zoeller, Journal of Rheology, 1993. (6): p. 1225-1235.

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