

## Thin Film

Room: 305 - Session TF-MoA

### Self-Assembled Monolayers, Layer-by-Layer Assemblies, and Hydrophobic/Amphiphobic Thin Films

Moderator: Subhadra Gupta, University of Alabama

2:40pm **TF-MoA3 Embedded Dipole in Alkanethiolate Self-Assembled Monolayers: Electronic Structure and Work Function Effects**, *Swen Schuster*, Heidelberg University, Germany, *N. Sullivan, O. Cabarcos*, Pennsylvania State University, *I. Hehn*, Graz University of Technology, Austria, *J.-F. Morin*, Université Laval, Canada, *E. Zofer*, Graz University of Technology, Austria, *M. Zharnikov*, Heidelberg University, Germany, *D.L. Allara*, Pennsylvania State University

Self-assembled monolayers (SAMs) bonded to metal-electrodes are frequently used to modify charge-carrier injection and also serve as prototypical systems for studying charge transport processes through molecular assemblies. Usually, control over charge-carrier injection is achieved by use of the terminal dipolar groups (terminal dipole) comprising the SAM-ambient interface. But this architecture affects the growth mode of an organic semiconductor (in the standard device configuration) entangling it with the dipole control. In contrast, for the molecules with an embedded dipolar element, the dipole control and the chemistry at the SAM-ambient interface are decoupled. In this context, we studied a series of SAMs on Au{111} prepared from the mid-chain ester functionalized thiols,  $\text{HS}(\text{CH}_2)_m\text{CO}_2(\text{CH}_2)_n\text{CH}_3$  (CmECn) with different combinations of  $m$  and  $n$ , different dipolar group orientations, and partial deuteration for some of these films. Electronic properties were analyzed by high resolution x-ray photoelectron spectroscopy (HRXPS), near edge x-ray absorption fine structure spectroscopy, work function measurements, and theoretical simulations with supporting characterization by infrared spectroscopy and AFM. The presence of the ester moiety leads to the formation of a strong electric dipole layer with a component of  $\sim 1.05$  Debye normal to the surface for most of the CmECn SAMs and results in a strong electrostatic effect on the HRXPS spectra in which the C 1s photoelectron kinetic energies are consistently shifted by 0.7-1.0 eV between the alkyl segments below and above the embedded ester group. In addition, this group affects the work function of the entire assembly, with the direction of the change following the direction of the embedded dipole. There is however no perfect correlation between the behavior of the HRXPS spectra and the work function, which has to be understood with the help of theoretical simulations.

3:00pm **TF-MoA4 Formation of Highly Ordered Self-Assembled Monolayers of Alkynes on Au (111) Substrates**, *T. Zaba, A. Noworolska*, Jagiellonian University, Poland, *C.M. Bowers, B. Breiten, G.M. Whitesides*, Harvard University, *Piotr Cyganik*, Jagiellonian University, Poland

Self-assembled monolayers (SAMs) based on C-Au bonding and prepared by reaction of terminal  $n$ -alkynes ( $\text{HC}\equiv\text{C}(\text{CH}_2)_n\text{CH}_3$ ,  $n = 5, 7, 9$ , and 11) with Au(111) at elevated temperatures (60 °C), were characterized using scanning tunneling microscopy (STM), infra-red reflection absorption spectroscopy (IRRAS), X-ray photoelectron spectroscopy (XPS) and contact angle of water.<sup>1</sup> In contrast to previous spectroscopic studies<sup>2,4</sup> of this type of SAM, these combined microscopic and spectroscopic experiments confirm the formation of highly-ordered SAMs having packing densities and molecular chain orientations very similar to those of alkanethiols on Au(111). Physical properties—hydrophobicity, high surface order, and packing density—also suggest that SAMs of alkynes are similar to SAMs of alkanethiols. The preparation of high-quality SAMs from alkynes requires careful preparation and manipulation of the reactants in a rigorously oxygen-free environment: trace quantities of oxygen lead to oxidized contaminants and disordered surface films. The influence of oxygen on the quality of the SAM is apparently not related to reaction of the Au-C bonds in a SAM with oxygen as suggested earlier,<sup>3</sup> but instead, suggests gold-catalyzed oxidation of the terminal acetylene in solution before incorporation into the SAM. Importantly, once clean alkyne based SAM is formed it becomes resistant to further oxidation in ambient conditions. This stability, together with high structural order, provides the basis for potential applications of this new type of SAM.

#### References

- (1) Zaba, T.; Noworolska, A.; Bowers, C. M.; Breiten, B.; Whitesides, G. M.; Cyganik, P. *submitted*, 2014
- (2) Zhang, S.; Chandra, K. L.; Gorman, C. B. *J. Am. Chem. Soc.* **2007**, *129*, 4876.

(3) McDonagh, A. M.; Zareie, H. M.; Ford, M. J.; Barton, C. S.; Ginic-Markovic, M.; Matisons, J. G. *J. Am. Chem. Soc.* **2007**, *129*, 3533.

(4) Scholz, F.; Kaletova, E.; Stensrud, E. S.; Ford, W. E.; Kohutova, A.; Mucha, M.; Stibor, I.; Michl, J.; Wrochem, F., *J. Phys. Chem. Lett.* **2013**, *4*, 2624.

3:40pm **TF-MoA6 Dynamic and Angle-Resolved XPS Analysis of Ultra Thin Polyelectrolyte Films Containing Metal Nanoparticles**, *Merve Taner-Camci\**, *S. Suzer*, Bilkent University, Turkey

Ultra thin polyelectrolyte layers have been constructed by sequential adsorption of PAH (polyallylamine hydrochloride) as cationic polyelectrolyte and PSS (polystyrene sulfonate) as anionic polyelectrolyte on silicon substrates using layer-by-layer assembly. Negatively capped AgCu nano-sized particles are incorporated as the outermost layer on the ultra thin film. The sequential order of adsorbed layers and nanoparticles are monitored by relative depth profile of the sample with respect to the intensity changes of corresponding photoelectron peaks, via Angle Resolved XPS analysis at different take off angles. Dynamic XPS analysis is performed under the application of external voltage bias with a known amplitude and frequency to control and probe the charging shifts, as well as polarity dependent intensity changes. The shifts in the binding energy position and the intensity fluctuations of photoelectron peaks reveal information about the relative position of the adsorbed polyelectrolyte layers, as well as proximity of atomic constituents of the nanoparticles.

4:00pm **TF-MoA7 Growth Ambient Dependent and Photoinduced Reversible Wetting Property of Indium Oxide Nanowires**, *Kavita Yadav, B.R. Mehta, J.P. Singh*, Indian Institute of Technology Delhi, India

In recent years, production of materials with tunable wetting properties is of immense interest. The extreme water repellent property of superhydrophobic surfaces and complete water spreading on superhydrophilic surface allow them to have considerable technical potential for various applications. The wetting properties of the materials can be explained by their surface chemistry and topographical structures.

In this report, we demonstrate that the growth ambient induced drastic change in wetting properties of indium oxide (IO) nanowires. The IO nanowires were synthesized by using chemical vapor deposition method where Ar gas (200 sccm) was used as carrier gas. The deposition parameters were calibrated in such a way to obtain nanowire morphology. Three different ambient conditions were used for growth of IO nanowires; (a) Ar gas mixed with water vapors, (b) only Ar gas and (c) Ar gas mixed with hydrogen gas (50 sccm) and keeping other deposition parameters constant. The Scanning electron microscope (SEM) images confirm that all the three samples have nanowires like morphology. The diameter and length of nanowires ranges from 50 - 120 nm and 6 - 15  $\mu\text{m}$ . The contact angle measurements were done on all the three samples. It is found that the nanowires prepared in presence of Ar gas mixed with water vapors (oxidising ambient) are superhydrophilic in nature with contact angle of  $8^\circ \pm 5^\circ$ . The IO nanowires synthesized in presence of only Ar gas are hydrophobic in nature with contact angle of  $144^\circ \pm 4^\circ$  whereas the IO nanowires synthesized in presence of Ar gas mixed with  $\text{H}_2$  gas (reducing ambient) are superhydrophobic in nature with contact angle of  $168^\circ \pm 2^\circ$  and water droplet rolling downward with a roll-off angle of  $3^\circ$  over the superhydrophobic surface. The mechanism behind the drastic change in contact angle on IO nanowires prepared in different growth ambient is examined by using photoluminescence (PL) and electron paramagnetic resonance (EPR) measurements. The mechanism of change in wetting properties of IO nanowires has been proposed and can be attributed as on the reduced surface where oxygen vacancy are more, only molecular water is stable and absorb weakly. This is most likely because of the lack of surface oxygen that could accept hydrogen from dissociated water or decrease water dissociation probability and hence the surface is superhydrophobic. Whereas the sample prepared in oxidizing ambient have more surface oxygen and hence both molecular and dissociative adsorption of water is possible results in superhydrophilic surface. The photoinduced reversible wetting properties of IO nanowires (sample b) are also studied.

4:20pm **TF-MoA8 Ultralow Friction and Adhesion on Fluorinated Covalently Surface-Bound Polymer Brushes**, *S. Pujari, N. Bhairamadgi, Han Zuilhof*, Wageningen University, Netherlands

For an ever increasing range of applications, such as in MEMS and NEMS, highly stable surfaces with minimal adhesion and friction are desired. In the current paper we present a method to achieve such polymer surfaces via a

\* TFD James Harper Award Finalist

combination of high-density attachment of surface-bound initiators on the Si(111) surface followed by a surface-initiated ATRP reaction with a series of fluorine-rich methacrylate monomer. Subsequently, the adhesion and friction forces were determined using colloidal probe scanning force microscopy. The resulting surfaces display the lowest adhesion force and friction coefficient in air currently reported for any flat surface, which is for example about 1 order of magnitude less than teflon, yet with an appreciably higher chemical and mechanical stability. The presentation will focus on preparation and characterization (both structural and tribological) of these surface-bound polymer brushes, and outline the potential of such minimally interacting surfaces.

4:40pm **TF-MoA9 Proton Conductive Crystalline Coatings by Initiated Chemical Vapor Deposition**, *Anna Maria Coclite, C. Ranacher*, Graz University of Technology, Austria

Proton conductive copolymers of perfluorodecylacrylate (PFDA) and methacrylic acid (MAA) are synthesized by initiated Chemical Vapor Deposition (iCVD). The MAA provides the –COOH groups useful to conduct protons, while the PFDA is responsible for creating the hydrophobic backbone to stabilize the structure during tests in water. The ultimate goal is to use these copolymers as proton exchange membranes in fuel cells. Preliminary experiments have shown that proton conductivities in the range of 70 mS/cm can be reached with these copolymers.<sup>1</sup> The aim of the new research is to study the effect of preferred crystallographic orientation on the proton conductivity and water / temperature stability of the copolymers. Preferred crystallographic orientation (texture) in thin films frequently has a strong effect on the properties of the materials and it is important for stable surface properties. Poly-PFDA has a high tendency to give organized molecular films. Crystalline poly-PFDA have been fully obtained also by iCVD.<sup>2</sup> The degree of crystallinity and the preferred orientation of the perfluoro side chains, either parallel or perpendicular to the surface, can be controlled by tuning the CVD process parameters (i.e. initiator to monomer flow rate ratio, filament temperature, and substrate temperature). Super-hydrophobicity (advancing water contact angle, WCA, of 160°, low hysteresis of 5°), and oleophobicity (advancing CA with mineral oil of 120°) were achieved.<sup>3</sup> Low water contact angle hysteresis was obtained with high crystallinity, particularly when the orientation of the crystallites resulted in the perfluoro side groups being oriented parallel to the surface. The latter texture resulted in smoother film (RMS roughness < 30 nm) than the texture with the chains oriented perpendicularly to the surface. This can be very advantageous for our application that require smooth but still crystalline films. When the PFDA is copolymerized with MAA, the degree of crystallinity decreases and therefore also the stability in water, but the proton conductivity increases due to the higher number of acid groups embedded in the structure. A good trade-off has been obtained when using 20% of MAA in the gas feed.

<sup>1</sup> A.M. Coclite et al., *Polymer*, 2013, 54, 24-30

<sup>2</sup> A. M. Coclite et al., *Adv. Funct. Mater.* 2012, 22, 2167–2176

<sup>3</sup> A. M. Coclite et al., *Adv. Mater.* 2012, 24, 4534–4539

5:00pm **TF-MoA10 Tailoring Polymeric Structures on Surfaces for Lubrication**, *Nicholas Spencer*, ETH Zürich, Switzerland **INVITED**

Nature generally lubricates its tribosystems in water, using sugar chains for lubricity, immobilized on a protein backbone that links them to the surface. These glycoproteins function by being able to immobilize water near the sliding surfaces. Man's attempts to mimic this behavior have involved end-grafted, hydrophilic polymers, and much has been published on the use of poly(ethylene glycol) (PEG) to this end. Man-made machines are more challenging to lubricate than those in nature, since they generally involve hard-hard contact, which nature usually avoids. PEG has been useful as a model system for aqueous lubrication, but has certain inherent problems, including a lack of stability. This presentation will therefore focus on "life after PEG", covering alternative water-compatible, polymer-brush systems, those created by grafting-from methods, and finally the extension of these approaches into a non-aqueous environment: oil.

# Authors Index

**Bold page numbers indicate the presenter**

— **A** —

Allara, D.L.: TF-MoA3, 1

— **B** —

Bhairamadgi, N.: TF-MoA8, 1

Bowers, C.M.: TF-MoA4, 1

Breiten, B.: TF-MoA4, 1

— **C** —

Cabarcos, O.: TF-MoA3, 1

Coclite, A.M.: TF-MoA9, **2**

Cyganik, P.: TF-MoA4, **1**

— **H** —

Hehn, I.: TF-MoA3, 1

— **M** —

Mehta, B.R.: TF-MoA7, 1

Morin, J.-F.: TF-MoA3, 1

— **N** —

Noworolska, A.: TF-MoA4, 1

— **P** —

Pujari, S.: TF-MoA8, 1

— **R** —

Ranacher, C.: TF-MoA9, **2**

— **S** —

Schuster, S.: TF-MoA3, **1**

Singh, J.P.: TF-MoA7, 1

Spencer, N.D.: TF-MoA10, **2**

Sullivan, N.: TF-MoA3, 1

Suzer, S.: TF-MoA6, 1

— **T** —

Taner-Camci, M.: TF-MoA6, **1**

— **W** —

Whitesides, G.M.: TF-MoA4, 1

— **Y** —

Yadav, K.: TF-MoA7, **1**

— **Z** —

Zaba, T.: TF-MoA4, 1

Zharnikov, M.: TF-MoA3, 1

Zojer, E.: TF-MoA3, 1

Zuilhof, H.: TF-MoA8, **1**