

Monday Morning, October 19, 2015

Thin Film

Room: 111 - Session TF+AS+SS-MoM

Self-Assembled Monolayers, Layer-by-Layer, etc.

Moderator: Han Zuilhof, Wageningen University, Netherlands

8:20am **TF+AS+SS-MoM1 The Effects of Embedded Dipoles in Aromatic Self-Assembled Monolayers**, *Sven Schuster*, Universität Heidelberg, Germany, *T. Abu-Husein*, Universität Frankfurt, Germany, *D.A. Egger*, *I. Hehn*, Graz University of Technology, Austria, *M. Kind*, Universität Frankfurt, Germany, *E. Zojer*, Graz University of Technology, Austria, *A. Terfort*, Universität Frankfurt, Germany, *M. Zharnikov*, Universität Heidelberg, Germany

Self-assembled monolayers (SAMs) are frequently used as intermediate films to modify charge-carrier injection from metal-electrodes into an organic semiconductor. This is usually achieved by use of the terminal dipolar groups comprising the SAM-ambient interface and affecting, at the same time, the growth chemistry of the semiconductor. Here we suggest an alternative approach, viz. embedding dipolar element into the molecular backbone, which allows decoupling the dipole control and the interfacial chemistry. As molecular backbone we use oligophenyl moiety which provides a suitable structural match to most organic semiconductors. As polar unit we use pyrimidine, varying its orientation in the molecular backbone and, consequently, the direction of the embedded dipole moment. The electronic and structural properties of these embedded-dipole SAMs are thoroughly analyzed using a number of complementary characterization techniques combined with quantum-mechanical modeling. We show that such mid-chain substituted monolayers are highly interesting from both fundamental and application viewpoints, as the dipolar groups are found to induce a potential discontinuity inside the monolayer, electrostatically shifting the energy levels in the regions above and below the dipoles relative to one another. These SAMs also allow for tuning the substrate work function in a controlled manner independent of the docking and interfacial chemistry. In addition, a mixture of the embedded-dipole molecules with opposite orientations of dipoles makes possible a fine tuning of the work function between the ultimate values, associated with a particular dipole orientation. Quantum-mechanical modeling in conjunction with x-ray photoelectron spectroscopy experiments provides insight into the molecular organization of such mixed monolayers.

8:40am **TF+AS+SS-MoM2 IR Spectroscopic studies of Molecular Thin Films exhibiting Spontaneous Dipole Alignment**, *Alexander Rosu-Finsen*, Heriot-Watt University, UK, *J. Lasne*, Heriot-Watt University, France, *A. Cassidy*, *D. Field*, Aarhus University, Denmark, *M.R.S. McCoustra*, Heriot-Watt University, UK

In recent years, observations of the presence of a spontaneous and powerful static electric field within thin films of molecular solids have been reported by Field and co-workers [1]. These electric fields, which can approach 10^8 V m⁻¹ or more, are believed to arise from alignment of the molecular dipoles in the thin films. Seeking to provide an independent means of observing this phenomenon of the "spontelectric phase", the first new electrically-unique, structural phase to have emerged in decades, we have used reflection-absorption infrared spectroscopy (RAIRS) to investigate thin films of nitrous oxide (N₂O). The presence of a static electric field within the thin film, the defining characteristic of spontelectrics, is demonstrated through the observed temperature dependence of longitudinal-transverse optical (LO-TO) splitting in RAIR spectra, using an analysis based on the vibrational Stark effect [2]. Tentative evidence for the surface-templating of the growth of the spontelectric phase will be presented from RAIRS studies of solid carbon monoxide (CO) on a range of water substrates (porous amorphous solid water, compact amorphous solid water and crystalline water) [3].

[1] Spontaneous electric fields in solid films: spontelectrics. D. Field, O. Plekan, A. Cassidy, R. Balog, N.C. Jones and J. Dunger, *Int. Rev. Phys. Chem.*, 2013, **32**, 345-392.

[2] Spontaneously electrical solids in a new light. J. Lasne, A. Rosu-Finsen, A. Cassidy, M. R. S. McCoustra and D. Field, *Phys. Rev. Lett.*, submitted.

[3] Templating dipole alignment in solid carbon monoxide on water ice surfaces. A. Rosu-Finsen, J. Lasne, A. Cassidy, D. Field and M. R. S. McCoustra, *Phys. Rev. Lett.*, in preparation.

9:00am **TF+AS+SS-MoM3 Coordination-Based Molecular Assemblies as Electrochromic Materials: Ultra-High Switching Stability and Coloration Efficiencies**^[1], *Michal Lahav*, Weizmann Institute of Science, Israel

Layer-by-Layer (LbL) deposition, combined with metal-ligand coordination, has served as a powerful tool for generating functional architectures.^[2] Such systems might find interesting applications in molecular electronics, sensor, solar cells and data storage. More significantly, owing to their interesting electrochromic (EC) behavior, they are promising candidates for use in smart windows and display devices. In this study we used a dip-coating process to generate molecular assemblies (MA) from metal polypyridyl complexes cross-linked with PdCl₂. These polypyridyl complexes are considered ideal chromophores for fabricating electrochromic materials, due to their excellent stability and light absorption that greatly depends on their oxidation state.^{[3],[4]} The number of pyridine moieties of the chromophores is varied to control (i) the materials' stability, (ii) color, (iii) redox-chemistry, and (iv) the film growth (i.e., linear vs. exponential). We also observed that minor structural differences (i.e., the pyridine-bipyridine bond order) at the molecular level become apparent when the stability and electrochromic properties are examined (Figure 1). The MAs exhibit high coloration efficiencies and are extremely stable: they are thermally robust and have exceptionally high (spectro)electrochemical activity. Furthermore, we demonstrated the formation of a first-generation solid-state set-up.^{[1],[5]}

1) S. Shankar, M. Lahav, M. E. van der Boom, *J. Am. Chem. Soc.* **2015**, *137*, Just Accepted Manuscript.

2) R. J. Mortimer, *Annu. Rev. Mater. Res.*, **2011**, *41*, 241.

3) G. de Ruiter, M. Lahav, M. E. van der Boom, *Acc. Chem. Res.*, **2014**, *47*, 3407-3416.

4) G. de Ruiter, M. Lahav, H. Keisar, M. E. van der Boom, *Angew. Chem., Int. Ed.* **2013**, *52*, 704-709.

5) M. E. van der Boom, M. Lahav, S. Shankar, US Patent 61/906,565, **2013**.

9:20am **TF+AS+SS-MoM4 New Approaches to the Preparation of Well-defined Metal Films on Top of Self-assembled Monolayers**, *Michael Zharnikov*, Universität Heidelberg, Germany

Self-assembled monolayers (SAMs) can be potentially used as ultrathin insulating dielectric layers or intermediate films in different electronic and spintronic devices. Whereas the bottom electrode in such assemblies is represented by the metal substrate, the top electrode should be prepared at the SAM-ambient interface. Regrettably, the formation of a well-defined metal film on top of the SAMs is a non-trivial task, since the metal atoms deposited onto the SAM-ambient interface do not stay there, but penetrate into the monolayer and diffuse to the metal substrate following a strong thermodynamical drive. Here I discuss three new approaches to suppress the above penetration and diffusion, taken a representative ferromagnetic metal, nickel, as a test adsorbate. The first approach relies on irradiation-induced cross-linking of a thiol-substituted aromatic SAM. Whereas 2D-polymerization of such a SAM prevents penetration of the metal atoms into the monolayer, the thiol groups at the SAM-ambient interface serve as nucleation centers for the growing "top" film. The second approach, relying on SAMs of perfluoroterphenyl-substituted alkanethiols, utilizes a chemical reaction between the SAM constituents and adsorbate atoms. The primary process is the Ni mediated loss of fluorine atoms followed by extensive cross-linking between the partly defluorinated molecular backbones. The stability of these backbones and the rapid development of the cross-linking are the key components to hinder the metal penetration. Finally, the penetration of deposited metal atoms into a SAM can be nearly completely inhibited by the preliminary formation of palladium-chloride seeding layer at the SAM-ambient interface. The palladium atoms in the seeding layer serve as nucleation centers for the growing metal film, staying at its bottom during the growth. In contrast, the chlorine atoms are transferred from palladium to the deposited metal, staying on the top of the growing metal film and serving as surfactants.

9:40am **TF+AS+SS-MoM5 N-Heterocyclic Carbenes as Novel Ligands for Self Assembled Monolayers on Gold**, *Cathleen Crudden*, Queen's University, Canada **INVITED**

The use of N-heterocyclic carbenes (NHCs) to modify homogeneous metal catalysts is widespread, however despite the versatility of these complexes, the high metal-NHC bond strength and oxidative stability of NHC-ligated metals, and the ease of synthesis of NHCs, there have been only a handful of reports of mostly ill-defined surfaces functionalized by NHCs.

We will describe the the use of NHCs to form self-assembled monolayers on gold surfaces. In particular, films prepared by the deposition of 1,3-dihydro- 1,3-bis(isopropylbenzimidazol-2-ylidene), show molecular ordering on the surface and remarkable stability. They show no decomposition upon heating for 24 hrs in THF, in boiling in water for 24hrs or upon treatment with acid (pH 2) or base (pH 12). Incredibly, they even survive largely after 24 hr exposure to hydrogen peroxide. This remarkable increase in stability relative to thiol-based SAMs will greatly increase the number of reagents and conditions to which the SAMs can be exposed.

The use of these films in SPR-based biosensing will be described, as will novel methods for the preparation of such films that can be carried out in air on the bench top.

10:40am **TF+AS+SS-MoM8 Improved Stability of Ag Thin Films due to Several Organic Surface Monolayers**, *Midori Kawamura*, Kitami Institute of Technology, Japan, *C. Kudo, T. Sasaki, Y. Abe, K.H. Kim, T. Kiba*, Kitami Institute of Technology

Due to excellent physical properties, Ag thin films have been used as low-e coating, optical mirror, and so on. It is necessary to prevent degradation of the Ag films in air or humid atmosphere. For the purposes, it has been reported that several metal oxide nanolayers and organic monolayers are effective to make Ag thin films stable. Previously, we reported that modification of Ag films with 3-mercaptopropyltrimethoxysilane (MPTMS) monolayer can improve durability of the Ag films after environmental tests because strong bonds were formed between thiol moiety and Ag films, and also between silanol moiety and glass substrate. In the present study, we attempted to use other type of organic molecules, namely straight chain alkylthiols, such as 1-octadecanethiol (1-ODT), 1-dodecanethiol (1-DT) for protection of Ag film surface and compared with MPTMS.

Ag thin films (10nm) were deposited on clean glass substrates by vacuum evaporation. Then monolayer of 1-ODT and 1-DT were formed over the Ag thin films by solution method. The samples were kept in a constant temperature and humidity chamber (40 degree Celsius and 90 RH%) for a week. The electrical resistance, surface morphology, optical transmittance were measured before and after the test. Ag film without the monolayer, and that with MPTMS were also examined for comparison.

The surface roughness of the Ag film without the monolayer drastically increased from 2.7 nm to 27 nm after the test. However, the increase was within 1nm on Ag films with 1-DT and 1-ODT surface layers. These changes were smaller than that on Ag film with MPTMS surface layer. By the measurement of electrical resistivity, it was found that increase in the resistivity after the test was very much suppressed in the Ag film with these monolayers. In addition, optical transmittance measurement showed that transmittance spectrum of Ag films with these monolayers did not change after the test. These results accord with the Ag film morphology change. Consequently, excellent passivation effect of 1-DT and 1-ODT surface monolayers on Ag films was confirmed.

11:00am **TF+AS+SS-MoM9 Electronic Structures of the Biaxially-strained GaSb(111) Films**, *Takuya Hatayama*, The University of Electro-Communications (UEC-Tokyo), Japan, *A. Akaishi*, The University of Electro-Communications (UEC-Tokyo), *J. Nakamura*, The University of Electro-Communications (UEC-Tokyo), Japan

III-V compound semiconductors have been extensively researched as alternative channel materials of complementary metal-oxide-semiconductor devices because of their superior carrier mobility[1]. In particular, GaSb is one of the promising p-channel materials, because its hole transport properties are significantly improved compared to Si. Recently, Ohtake *et al.* Have reported that high-quality GaSb films can be epitaxially grown on the Si(111) substrate using the InAs buffer layer[2]. The lattice constant in the plane of growth for the thin GaSb epilayer inherits the lattice constant of InAs, causing an inherent strain in the GaSb film. As a result, the electronic structure of the GaSb film can be modified. In this study, we evaluate the electronic properties of the strained GaSb bulk and the (111) films, especially the band gap formation, the effective mass, and the electronic conductivity, using first-principles calculations within the density functional theory. In general, the local density approximation (LDA) is commonly applied to the exchange correlation term. However, it has been well-known that the band gap of semiconductors is significantly underestimated with LDA. In order to rectify the underestimation of the band gap and to correctly evaluate electronic dispersions at band edges, we use the hybrid functional proposed by Heyd-Scuseria-Ernzerhof (HSE06) for the exchange-correlation term[3]. The spin-orbit interaction is also included.

We assume the biaxial strain parallel to the GaSb (111) plane. For the bulk with a direct band gap at ambient pressure, GaSb becomes an indirect band gap material under the compressive biaxial strain. The biaxial strain makes the twofold-degenerate heavy-hole and light-hole bands split into two bands at the Gamma point of the valence band. Interestingly, under the biaxial tensile strain, the effective mass of holes becomes anisotropic. We will also

report on changes in electronic properties of the GaSb (111) ultrathin films under the biaxial strain.

[1] J. A. del Alamo, *Nature* **479**, 317 (2011)

[2] A. Ohtake, T. Mano, N. Miyata, T. Mori, and T. Yasuda, *Appl. Phys. Lett.* **104**, 032101 (2014)

[3] J. Heyd, G. E. Scuseria, and M. Ernzerhof, *J. Chem. Phys.* **118**, 8207 (2003); *ibid* **124**, 219906 (2006)

11:20am **TF+AS+SS-MoM10 How to Repel Polymer Adsorption on Flat Surfaces?**, *Zhanhua Wang, S.P. Pujari, M.M.J. Smulders, H. Zuilhof*, Wageningen University, Netherlands

Organic monolayers or polymer brushes, often in combination with surface structuring, are widely used to prevent nonspecific adsorption of polymeric or biological material on sensor and microfluidic surfaces. Here we show for the first time how robust, covalently attached alkyne- derived monolayers or ATRP-produced polymer brushes, with a varying numbers of fluorine atoms, on atomically flat Si(111), effectively repel a wide range of apolar polymers without the need for micro- or nanostructuring of the surface. We have studied the antifouling property of fluoro-hydro monolayers and of fluorine-containing polymer brushes towards a range of commonly used polymers/plastics with comparable molecular weight in non- aqueous solvent, and have investigated the effect of polymer molecular weight on the fouling behavior. These studies relied on a range of characterization methods: wettability studies, ellipsometry, X- ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). We developed a novel surface morphology survey by AFM characterization that can accurately quantify the degree of fouling.

These studies consistently displayed that especially the mono-fluorinated (F1) monolayer shows excellent anti- fouling behavior, even more so than e.g. corresponding monolayers with perfluorinated alkyl tails. In this presentation the causes of this unprecedented and surprising finding are discussed. Second, we will focus on polymer brush properties that further reduce the adsorption of polymers. These findings and analysis offer significant potential for antifouling applications of ultrathin and covalently bound fluorine- containing coatings for a range of micro- and nanotechnological applications.

11:40am **TF+AS+SS-MoM11 Symmetric Attachment of Annulated Aromatic Hydrocarbons in Self-assembled Monolayers by Use of Oxazoles**, *C. Partes*, University of Frankfurt, Germany, *S. Schuster, T. Wächter*, University of Heidelberg, Germany, *Martin Kind*, University of Frankfurt, Germany, *M. Zharnikov*, University of Heidelberg, Germany, *A. Terfort*, University of Frankfurt, Germany

Self-assembled monolayers (SAMs) have proven to be powerful tools for tuning surface properties because of the uncomplicated method of their preparation and the high variability of their organic moieties. The suitability of SAMs in applications like, e.g., organic electronics is frequently investigated. An aim for the use of SAMs is the reduction of injection barriers that occur at the interfaces between organic semiconductors and technologically relevant substrates like gold or silicon.

A SAM ideal for this purpose should exhibit a high vertical conductivity. In view of this, we investigated several aromatic and araliphatic SAMs, e.g. terphenyl-terminated monolayers on gold [1]. In a more recent ansatz, we have examined SAMs bearing annulated moieties such as anthracene, which in contrast to oligophenyls are entirely planar [2]. However, as a consequence of the asymmetric substitution of anthracene to the thiol anchor group it is hardly possible to alter the tilt angle of these thiolate molecules within the SAMs [2].

To overcome this drawback, we extended the annulated system of the SAM-forming thiols with an oxazole unit, which allows for a quasi-symmetric attachment to the anchor group. This restores the possibility to influence the tilt angle of the aromatic units using the so-called odd-even effect in SAMs.

Here, we like to present preliminary results on preparation and structural properties of SAMs made from aromatic oxazole thiols on gold surfaces.

REFERENCES

[1] Shaporenko, A.; Brunnbauer, M.; Terfort, A.; Grunze, M.; Zharnikov, M./J. Phys. Chem. B/108, 14462-14469 (2004).

[2] Dauselt, J.; Zhao, J.; Kind, M.; Binder, R.; Bashir, A.; Terfort, A.; Zharnikov, M./J. Phys. Chem. C/115, 2841-2854 (2011).

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