

# Tuesday Afternoon, October 23, 2018

## Thin Films Division

### Room 102A - Session TF+SS-TuA

#### Organic/Inorganic Materials and Interfaces

Moderator: Matthew Richard Linford, Brigham Young University

**2:20pm TF+SS-TuA-1 Chemical Interactions at Hybrid Interfaces: An In Situ Investigation of Organic/Inorganic Systems, Sven Pletincx**, Vrije Universiteit Brussel, Belgium; *L Trottochaud*, Lawrence Berkeley Lab, University of California, Berkeley; *L Fockaert, M Meeusen, A Mol*, Technical University Delft, Netherlands; *H Bluhm*, Lawrence Berkeley Lab, University of California, Berkeley; *H Terryn, T Hauffman*, Vrije Universiteit Brussel, Belgium

The durability of hybrid systems is mainly determined by the different phenomena occurring at the organic/inorganic interface. However, analyzing this solid/solid or liquid/solid interface under technologically relevant conditions is challenging. Recently, the *in situ* investigation of these so-called buried interfaces is done by monitoring ultrathin polymer films onto a metal oxide substrate by ambient-pressure photoelectron spectroscopy (APXPS).<sup>1,2</sup> Here, we show that APXPS with a conventional X-ray source can be used to study the effects of water exposure on the interaction of different acrylic coatings with aluminum oxide.

The deposition of this nanometer thin overlayer is often carried out by reactive adsorption from dilute polymer solutions. However, the influence of the solvent on the metal oxide chemistry is seldom taken into account in interface studies. An integrated spectroelectrochemical setup of ATR-FTIR Kretschmann and Odd Random Phase multisine Electrochemical Impedance Spectroscopy (ORP-EIS) allows to monitor the influence of the solvent on the metal oxide surface. An aluminum layer is sputtered on an IR transparent crystal, the IR signal at the interface is amplified because of the Kretschmann effect, and a near-interface spectrum of the organic/oxide surface is obtained. The occurring interface processes can be followed with infrared spectroscopy while simultaneously, the PVD layer acts as a working electrode. This allows to determine the electrochemical properties of the overall hybrid system, studied by ORP-EIS.<sup>3</sup>

After the characterization of the solvent interactions, *in situ* ATR-FTIR Kretschmann/ORP-EIS is used to study the effect of an electrolyte on an acrylic polymer/metal oxide system. This way, we have direct access to the interface, and the influence of an above-the-polymer electrolyte (i.e. H<sub>2</sub>O) can be probed. Also the study of covalent bonding, such as the interfacial interactions of silane adhesion promoters are investigated. This work shows that by using ultrathin films and a set of recently developed techniques, it is possible to non-destructively and *in situ* probe interfacial changes in hybrid systems.

1. Pletincx, S. *et al.* In Situ Characterization of the Initial Effect of Water on Molecular Interactions at the Interface of Organic/Inorganic Hybrid Systems. *Sci. Rep.* **7**, 45123 (2017).
2. Pletincx, S. *et al.* Unravelling the Chemical Influence of Water on the PMMA/Aluminum Oxide Hybrid Interface In Situ. *Sci. Rep.* **7**, 13341 (2017).
3. Hauffman, T. *et al.* Measuring the adsorption of ethanol on aluminium oxides using odd random phase multisine electrochemical impedance spectroscopy. *Electrochim. commun.* **22**, 124–127 (2012).

**2:40pm TF+SS-TuA-2 Microscopic and Spectroscopic evidence of Odd-Even Effect in Self-Assembled Monolayers of Biphenyl-Substituted Fatty Acid on Ag(111), Anna Krzykawska**, Jagiellonian University, Polska; *P Cyganik, M Szwed, J Ossowski*, Jagiellonian University, Poland

Self-assembled monolayers (SAMs) have been broadly studied as a model system for inorganic-organic interface in molecular electronics and biosensing devices. Current standard in SAMs formation is based on using sulfur as an anchoring group to the metal substrate. In our recent paper<sup>1</sup> we have indicated that by replacing thiol headgroup by carboxylic, a highly interesting alternative is obtained, particularly when 2D ordering, SAM fabrication time and stability in ambient conditions are of great importance. Following this first observation made for a specific system, in the current work we have investigated a homolog series of SAMs based on biphenyl-substituted fatty acids on Ag(111) in the form of (C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>-(CH<sub>2</sub>)<sub>n</sub>-COO/Ag (BPnCOO/Ag, n = 1-4). The series of experiments were carried out using infrared reflection absorption spectroscopy (IRRAS), scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS). The results of this combined microscopic and spectroscopic analysis demonstrate very strong dependence of the structural properties on the

number of the CH<sub>2</sub> groups in the short aliphatic linker. Monolayers with *n* = even show highly ordered and stable structures. In contrast, SAMs with *n* = odd have disordered liquid-like structure with more canted orientation of the molecular backbone and the carboxylic headgroup, which results in lower packing density and film thickness compared to the even-numbered SAMs. By comparing obtained results with former odd-even effects reported for analogues SAMs based on thiols and selenols<sup>3,4</sup>, a common, qualitative model relating the odd-even effect to the monolayer stability and structure will be discussed. Our results demonstrate that for BPnCOO/Ag, this odd-even effect is particularly strong and fully controls the ability of molecules to form highly ordered structures. This observation seems to be of key importance for the design of SAMs based on the carboxylic group, which, for correctly designed molecules, forms much better 2D-ordered structures compared to commonly used thiols.

#### References

- [1] K rzykawska, A.; Ossowski, J.; Zaba, T.; Cyganik\*, P., *Chem. Comm.* **2017**, 53, 5748-5751
- [2] Krzykawska, A.; Szwed, M.; Ossowski, J.; Cyganik\*, P., *J. Phys. Chem. C* **2018**, 122, 919-928
- [3] Cyganik, P.; Buck, M.; Azzam, W.; Wöll\*, C., *J. Phys. Chem. B* **2004**, 108, 4989-4996
- [4] Cyganik\*, P.; Szelagowska-Kunstman, K.; Terfort, A.; Zharnikov,M., *J. Phys. Chem. C* **2008**, 112, 15466-15473

**3:00pm TF+SS-TuA-3 CVD of Thin Polymer Films for Engineered Material Properties, AnnaMaria Coclite**, Graz University of Technology, Austria

#### INVITED

Functional thin films offer innovative solutions for many technological applications: organic electronics, smart devices for biotechnology, microfluidics, membrane technology, sensors and drug delivery systems. The development of functional thin films, engineered to achieve all the desired properties, requires advanced growth techniques. The development of dry growth methods - based on vacuum- aims to complement and enlarge the applicability of functional thin films to fields where the presence of solvent is detrimental.

Successful results in terms of rationally designed micro- and nanoengineered materials will be demonstrated using as a case of study the growth of functional polymers by initiated CVD (iCVD). The high versatility of iCVD in driving application-specific properties into the material, creating a platform for the implementation of polymeric coatings into device fabrication will be discussed.

Layered nanostructures in proton conductive iCVD polymers were investigated though X-ray based methods. The polymers crystallize in a bilayer structure, perpendicular to the substrate surface, formed by perfluorinated pendant chains. Acid moieties were introduced to form ionic channels among the bilayers –parallel to the substrate surface- which can be responsible for proton conduction. This one-step polymerization process has the potential to manufacture inexpensive, high quality membranes for proton exchange membrane fuel cells.

Another case of study will be presented in the field of multi-stimuli-responsive materials. In particular, the material of interest in this case is a hydrogel that changes its size and shape when stimulated by light and humidity. Hydrogels are known for their dynamic swelling response to aqueous environments. A chemical functionalization of the hydrogel surface was performed to add other stimuli-responsive functionalities and obtain a smart material that responds to two stimuli. Modifying the hydrogel surface with solution-based methods is often problematic because of the damages caused by the permeation of solvents in the hydrogel. This issue is completely bypassed by the use of solvent-free techniques, like iCVD.

**4:20pm TF+SS-TuA-7 Organosilicon Functionally Nanostructured Films as Engineered Interlayers for Hybrid Materials, Vladimir Cech**, Brno University of Technology, Czech Republic; *J Houdkova*, Institute of Physics, Academy of Sciences of the Czech Republic; *M Branecky, T Plichta*, Brno University of Technology; *J Zemek*, Institute of Physics, Academy of Sciences of the Czech Republic

Thin films of organosilicones synthetized in low-temperature plasma constitute a class of materials with a rich and varied scientific background. This class of materials in the form of hydrogenated amorphous carbon-silicon (a-CSi:H) films has a distinctive characteristic that distinguishes it from other thin films – the ability to vary and control the degree of organic/inorganic character and crosslinking of carbon-silicon network by

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appropriate choice of fabrication variables. Oxygen atoms can be incorporated in organosilicon film to form new chemical bonds (Si-O, C-O, C=O) and vary the mechanical properties of hydrogenated amorphous carbon-silicon oxide (a-CSiO:H) films by modifying the carbon-silicon network. However, a multilayer rather than single layer film can fulfill specific functions not only in sophisticated electronic, optical, mechanical, and biomedical devices, but also in hybrid materials (composites and nanocomposites) with controlled interphase.

Functional multilayer nanostructures with controlled distribution of mechanical properties across the nanostructure were constructed from oxygen-free (a-CSi:H) and oxygen-bound (a-CSiO:H) individual layers deposited at different effective power or pulse period from tetravinylsilane and tetravinylsilane in a mixture with oxygen gas, respectively, by plasma-enhanced chemical vapor deposition operated in pulsed mode. XPS depth profiling using argon cluster ion beams was used to determine the atomic concentration of carbon, silicon, and oxygen in individual layers forming the multilayer nanostructures with a total thickness of about 100 nm. The XPS analysis revealed that the oxygen-free layers were oxidized due to post-deposition oxidation in the ambient air. Oxygen was even diffused in an oxygen-bound layer, which was confirmed by repeated XPS depth profiling within three months after multilayer deposition. The upper oxygen-bound layer at the multilayer surface behaved as a barrier reducing oxygen diffusion. The high energy-resolution XPS spectra (C 1s, Si 2p, and O 1s) were analyzed to gain more insight into bonding species formed in functionally nanostructured film. This detailed analysis showed that oxygen atoms, originating from the ambient air, were bound in oxidized (a-CSi:H) layers forming the same bonding states as those in as-deposited oxygen-bound layers.

## 4:40pm TF+SS-TuA-8 Studying Electron Induced Chemical Changes of Hafnium Oxide-Methacrylate EUV Photoresists with *In Situ* IR Spectroscopy and Model Flat Surfaces, *Yasiel Cabrera, E Mattson, K Oyekan, Y Wang, Y Chabal*, University of Texas at Dallas

New development in extreme ultraviolet (EUV) photolithography, using 13.5 nm photons, has brought us closer to a new era of device fabrication with sub-10 nm nodes. In the last decade, there has been many significant contributions to the development of EUV lithography, but limitations in photoresist development has made it difficult to implement the technology. Another significant challenge arises from the reality that EUV scanners are very expensive and limited for academia purposes, which ultimately slow down the process in understanding important mechanistic details for optimization of EUV resist materials. In this work, we emulate industrial EUV ionizing photons/events with low energy 90 eV electrons, which are believed responsible for inducing chemistry. Here, we are presenting results for nanoclusters resist based on hafnium-oxide core capped with methacrylic acid ligands (HfMAA). Using a combination of *in situ* infrared (IR) spectroscopy and density functional theory (DFT) calculations, we establish an atomic-scale mechanistic picture for each step of a photo-lithography process. To further understand the chemical changes leading to solubility switching, we have also developed a model surface system by translating the 3D structure considered in an HfMAA thin films (< 30 nm thick on SiO<sub>2</sub>) to a 2D system comprised of a single methacrylic acid (MAA) monolayer grafted onto an ALD grown HfO<sub>2</sub> film. The model system allows us to explore three areas related to the nanocluster system: first IR spectroscopy shows that the model surface is a good representation of the HfMAA thin film by matching many of the IR modes observed; second, similar to HfMAA, 90 eV electron irradiation shows the formation of alkyl CH<sub>2</sub> groups on the surface, with the loss of carboxylate and C=C bonds in the MAA adlayer; third, by comparing with different metal-oxide surface (Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>) and different carboxylate ligands (isobutyric acid (IBA), and hydroxybenzoic acid (OHBA)), we have demonstrated that analogous metal oxide/adlayer combinations can be used as a comparative tool to survey optimal combinations of organic and inorganic compounds for resist development by quantitatively evaluating the role of metal centers in inducing reactions.

## 5:00pm TF+SS-TuA-9 Photoactivated Molecular Layer Deposition of Fluoropolymer Thin Films, *Richard Closser*, Stanford University; *M Lillethorup*, Radisurf Aps, Denmark; *D Bergsman, J Shi, S Bent*, Stanford University

Recent developments of organic thin-film technologies have highlighted the need for deposition techniques which allow for a high degree of control over film thickness and conformality. Many methods, such as chemical and physical vapor deposition, have made substantial progress towards meeting those requirements; however, molecular layer deposition (MLD)

may be the ideal candidate for future development. MLD is an organic vapor deposition technique that takes advantage of sequential, self-limiting surface reactions, analogous to atomic layer deposition (ALD), whereby thin-film polymers can be deposited with angstrom-level thickness control even onto high aspect-ratio features. There are inherent constraints, however, to the variety of chemistries available for MLD, due to its vapor-phase nature, which precludes the use of solvents and many catalysts. As a result, most MLD polymers contain heteroatom-type connectivities and do not include new carbon-carbon bonding moieties, thus preventing the formation of many of the most common commercially available polymers.

Here, we discuss a new approach to MLD, photoactivated molecular layer deposition (pMLD), a process which provides new pathways to forming carbon-carbon bonds. In pMLD, monomers are activated upon exposure to UV light to create metastable radicals, which are then reacted with alkenes in a step-wise polymerization. Self-limiting bifunctional precursors are chosen which limit the extent of homopolymerization while enabling layer-by-layer growth. In this work, an alternating hydrocarbon-fluorocarbon polymer was deposited via pMLD using bifunctional diiodofluoroalkanes and dienes. It was determined using ellipsometry that the deposition has a constant growth rate and displays saturation behavior. X-ray photoelectron spectroscopy (XPS) analysis indicates the formation of new carbon-carbon bonds. By using alternate monomer backbones, we show that the composition follows a nearly 1:1 monomer deposition ratio, an indication that homopolymerization is minimized. *In situ* XPS annealing shows the fluoropolymer exhibits high temperature stability up to 400 °C, similar to a pure polytetrafluoroethylene polymer. The films also display chemical resistivity to a variety of solvents, acids, and bases. Elemental mapping using Auger electron spectroscopy confirms that the fluoropolymer film can be patterned using a UV photomask. We also show that the pMLD film can be used for ALD inhibition, blocking up to 100 cycles of Pt ALD. The strategy described in this work enables a new scope of applications for MLD, whereby carbon-carbon bonds are formed, greatly expanding the MLD toolbox.

## 5:20pm TF+SS-TuA-10 Sputter-Deposited Porous Coatings for Solid Phase Microextraction, *Tuhin Roychowdhury, D Patel, M Linford*, Brigham Young University

Solid Phase Microextraction (SPME) is 'green method' for isolating target analytes from complex matrices. It works by placing a coated fiber near a sample such that the molecules of interest can be selectively extracted and concentrated. These captured species are then released into a chromatograph for separation, identification, and quantification. Popular, commercial SPME coatings suffer from various drawbacks that include solvent incompatibility, low capacity, limited lifetime, etc. These problems are addressed by our new class of SPME fibers that offer extraordinary capacity, sensitivity, and speed. Our approach includes sputtering silicon onto fiber substrates to produce columnar structures. These porous silicon nanostructures are further oxidized leading to a high density of silanol groups on their surfaces. We have now demonstrated that both silanes and ultrathin PDMS layers can be deposited on these surfaces. These coatings can be produced in various morphologies and thicknesses by manipulating the sputter and deposition conditions. For example, refractory materials like carbon can also sputtered onto these fibers to create porous morphologies, which should be beneficial for chromatography. The surfaces and materials generated for SPME in this project have been characterized by X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), spectroscopic ellipsometry (SE), time-of-flight secondary ion mass spectrometry (ToFSIMS), and wetting. The performance of our 2 μm thick, porous, sputtered coatings has been compared to that of a thicker (7 micron) commercial coating. Our fiber consistently outperforms the commercial fiber, showing significantly higher capacity for higher molecular weight polycyclic aromatic hydrocarbons (PAHs). PAHs are a significant environmental pollutant due to their toxicity and carcinogenicity. These results are not the end of what is possible. Based on our work in this area we are convinced that further significant improvements in extraction efficiency and selectivity are possible.

## 5:40pm TF+SS-TuA-11 Interfacial Electron Transfer of Ferrocene Immobilized onto Indium Tin Oxide through Noncovalent Interactions, *Caitlin Hanna, J Yang*, University of California, Irvine

Immobilization of molecular species onto electrode surfaces is a strategy for the modification of surface properties with molecular specificity. Attachment of molecular fuel forming catalysts to photovoltaic electrodes, for example, is a promising route to efficient solar fuel generation. Current attachment methods are synthetically difficult and can have adverse

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effects on the electrode performance. This report describes a non-covalent method for molecular immobilization onto indium tin oxide (ITO) surfaces. The fabrication, characterization, and electrochemical behavior of 1-pyrenylferrocene physisorbed onto ITO surfaces through  $\pi$ - $\pi$  interactions is described. X-ray photoelectron spectroscopy (XPS) and cyclic voltammetry confirm the attachment of 1-pyrenylferrocene to the surface and highlight the stability of the system for aqueous electrochemical applications. The electron transfer kinetics between the ITO electrode and non-covalently attached ferrocene are compared to the kinetics of covalently-bound ferrocene. The kinetic studies of electron transfer show that electron transfer is ten times faster for non-covalently attached ferrocene than for covalently attached ferrocene.

6:00pm TF+SS-TuA-12 Vapor Phase Infiltration of Polymers with Intrinsic Microporosity: Structure and Chemical Separation Performance, *Mark Losego, E McGuinness, F Zhang, R Lively*, Georgia Institute of Technology

Over 10% of the world's energy consumption goes to separating chemicals via thermal distillation. Membrane-based separation can drastically reduce these energy and financial costs, but membranes must be carefully designed to meet performance and durability needs. Polymers of intrinsic microporosity like PIM-1 are emerging membrane materials of interest for industrial separations. These materials can be readily formed into films and/or fiber bundles for rapid chemical separation. However, PIM-1 swells in many solvents (e.g., ethanol) and can suffer from long-term porosity collapse. We have been investigating the vapor phase infiltration of these PIM-1 materials with inorganic constituents to improve performance and long-term stability. These studies have revealed a number of surprising observations including that these materials can be loaded to an excess of 30 wt% inorganics using a single VPI exposure dose despite no indication of chemical binding between the organic and inorganic constituents. We currently believe this loading is due to an intermediate binding state between the metalorganic precursors and the PIM-1's nitrile group. This binding state is sufficiently stable to withstand 2 days of inert gas purging, yet when exposed to an oxidant and removed from the reaction chamber no permanent chemical reactions between inorganic and PIM-1 can be detected by XPS, NMR, or FTIR. After infiltration, these organic-inorganic hybrid membranes show unprecedented performance for a PIM, fully capable of separating small molecules in ethanol solvents that should swell and collapse the polymer's pores.

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