

## Thin Film

Room: 10 - Session TF+EM+SS-ThA

### Applications of Self-Assembled Monolayers and Layer-by-Layer Assemblies

Moderator: M.R. Linford, Brigham Young University

2:00pm **TF+EM+SS-ThA1 Light-Directed Nanosynthesis: Near-Field Optical Approaches to Integration of the Top-Down and Bottom-Up Fabrication Paradigms**, *G.J. Leggett*, University of Sheffield, UK  
**INVITED**

The integration of top-down (lithographic) and bottom-up (synthetic chemical) methodologies remains a major goal in nanoscience. At larger length scales, light-directed chemical synthesis, first reported two decades ago, provides a model for this integration, by combining the spatial selectivity of photolithography with the synthetic utility of photochemistry. Work in our laboratory has sought to realise a similar integration at the nanoscale, by employing near-field optical probes to initiate selective chemical transformations in regions a few tens of nm in size. A combination of near-field exposure and an ultra-thin resist yields exceptional performance: in self-assembled monolayers, an ultimate resolution of 9 nm (ca. 1/30) has been achieved. A wide range of methodologies, based on monolayers of thiols, silanes and phosphonic acids, and thin films of nanoparticles and polymers, have been developed for use on metal and oxide surfaces, enabling the fabrication of metal nanowires, nanostructured polymers and nanopatterned oligonucleotides and proteins. Strategies based upon the use of nitrophenyl-based photocleavable protecting groups have enabled the introduction of synthetic chemical methodology into nanofabrication. Nanoscale control of chemistry over macroscopic areas remains an important challenge. Recently parallel near-field lithography approaches have demonstrated the capacity to pattern macroscopic areas at high resolution, yielding feature sizes of ca. 100 nm over an area four orders of magnitude larger; they have also demonstrated the ability to function under fluid, yielding feature sizes of ca. 70 nm in photoresist under water and suggesting exciting possibilities for surface chemistry at the nanoscale. Finally, the monolayer patterning methods we have developed are by no means restricted to near-field lithography; all that is required is a suitable means of confining the optical excitation. For example, SAM photochemistry has been combined with interferometric exposure to facilitate the fabrication of periodic nanostructures over macroscopic areas in fast, simple, inexpensive processes, underlining the versatility of photochemistry as a nanofabrication tool.

2:40pm **TF+EM+SS-ThA3 Molecular Layer Deposition (MLD) of Polymer Multiple Quantum Dots on TiO<sub>2</sub>**, *T. Yoshimura, S. Ishii*, Tokyo University of Technology, Japan

**[Introduction]** We previously proposed oxide-semiconductor-based sensitized solar cells, in which polymer multiple quantum dots (MQDs) are utilized for sensitizing layers, and fabricated the polymer MQDs on glass substrates by Molecular Layer Deposition (MLD) [1]. In the present study, we grew polymer MQDs on TiO<sub>2</sub> by MLD. The polymer MQD growth on TiO<sub>2</sub> was confirmed by photoluminescence (PL) spectra.

**[Proposed Solar Cells Sensitized by Polymer MQDs]** The proposed sensitized solar cell consists of an oxide semiconductor layer and polymer MQDs on the surface. The polymer MQD contains different-length quantum dots (QDs) in the backbone wire, and consequently, a wide absorption band is obtained by superposition of narrow absorption bands of the individual QDs. This spectral division with the narrow bands can reduce the energy loss arising from the heat generation due to excess photon energy in light absorption processes.

**[Absorption/Photoluminescence Spectra of Polymer MQDs]** Reference samples of poly-azomethine (AM) and polymer MQDs: OTPTPT, OTPT, and OT were grown on glass substrates by connecting terephthalaldehyde (TPA), *p*-phenylenediamine (PPDA), and oxalic dihydrazide (ODH) with designated orders using MLD. The QD lengths in OTPTPT, OTPT and OT are respectively ~3, ~2 and ~0.8 nm. With decreasing the QD length, while the absorption peak shifts to high-energy side due to the quantum confinement, the PL peak shifts to low-energy side due to the Stokes shift. Namely, in the order of poly-AM to OT, the electrons become highly localized to increase the surrounding atoms' displacement caused by the electron transitions, resulting in the Stokes shift enhancement.

**[Growth of Polymer MQDs on TiO<sub>2</sub>]** We performed MLD to grow poly-AM on ZnO and TiO<sub>2</sub> powder layers. A yellow film of poly-AM was observed on TiO<sub>2</sub>. For ZnO, however, no film growth was observed because

of weak hydrophilic characteristics of ZnO surfaces. We grew poly-AM and polymer MQDs of TO on the TiO<sub>2</sub> powder layers by MLD, and measured their PL spectra. The PL spectrum of TO was located at lower-energy side than that of poly-AM, which is parallel to the tendency observed in the PL spectra of the reference samples. From this result, it is concluded that polymer MQDs can be grown on TiO<sub>2</sub> by MLD as the sensitizing layers for solar cells.

[1] T. Yoshimura, R. Ebihara, A. Oshima, "Polymer Wires with Quantum Dots Grown by Molecular Layer Deposition of Three Source Molecules for Sensitized Photovoltaics," *J. Vac. Sci. Technol. A* **29**: 051510-1-6 (2011).

3:00pm **TF+EM+SS-ThA4 Thiol-yne Click Chemistry: Old Concept & New Applications in Surface Science**, *N.S. Bhairamadi, H. Zuilhof*, Wageningen University, Netherlands

Click chemistry reactions have opened new horizons in the field of surface chemistry, as these reactions are easy to perform on surfaces. A nice example is the addition of thiol moieties onto C=C bonds, which have been shown to be highly efficient, orthogonal to many other reactions, highly selective, etc. Recently we and others have shown that thiol-ene click reactions can be used efficiently for the modification of semiconductor surfaces and nanoparticles with a wide range of materials. In the current presentation we show an improved procedure involving C=C bonds, i.e. thiol-yne click reactions.

We modified oxide-free Si(111) surfaces with alkene-terminated and alkyne-terminated monolayers, and these surfaces were further modified with various thiols such as thioglycolic acid, thioacetic acid, thioglycerol, thio-β-D-glucose tetraacetate lactose and 9-fluorenylmethoxy-carbonyl cysteine by using thiol-ene and thiol-yne click reactions. Upon detailed surface analysis it was found that after some optimization the thiol-yne click reaction yielded 20 – 80 % more surface coverage compared to thiol-ene click reactions. Thus surface modification with thiol-yne click reactions promise to be the next step in surface-bound thiol click chemistry.

References:

1. Campos, M. A. C.; Paulusse, J. M. J.; Zuilhof, H., Functional monolayers on oxide-free silicon surfaces via thiol-ene click chemistry. *Chem. Commun.* 2010, 46 (30), 5512-5514.
2. Lowe, A. B.; Hoyle, C. E.; Bowman, C. N., Thiol-yne click chemistry: A powerful and versatile methodology for materials synthesis. *J. Mater. Chem.* 2010, 20 (23), 4745-4750.
3. Ruizendaal, L.; Pujari, S. P.; Gevaerts, V.; Paulusse, J. M. J.; Zuilhof, H., Biofunctional Silicon Nanoparticles by Means of Thiol-Ene Click Chemistry. *Chem. Asian J.* 2011, 6 (10), 2776-2786.
4. Wendeln, C.; Ravoo, B. J., Surface Patterning by Microcontact Chemistry. *Langmuir* 2012, 28 (13), 5527-5538.
5. Wendeln, C.; Rinnen, S.; Schulz, C.; Arlinghaus, H. F.; Ravoo, B. J., Photochemical Microcontact Printing by Thiol-Ene and Thiol-Yne Click Chemistry. *Langmuir* 2010, 26 (20), 15966-15971.

3:40pm **TF+EM+SS-ThA6 Attachment of Conjugated Diruthenium Alkynyl Compounds by Click Chemistry**, *S. Pookpanratana*, National Institute of Standards and Technology, *S.P. Cummings, T. Ren*, Purdue University, *C.A. Richter, C.A. Hacker*, National Institute of Standards and Technology

Attaching electrochemically-active molecules to a variety of different surfaces is of particular interest for applications in photovoltaic devices, catalysis, and molecular electronics. The family of diruthenium 2-anilinopyridinate (ap) molecules is redox active [1], which makes it an ideal candidate to incorporate on surfaces for molecular catalysis, photoelectrochemical cells for water splitting, and as an active component in molecular electronic devices. Often times, the attachment of a tailored-molecule requires the additional design challenge to incorporate a specific anchoring group (e.g., thiol). Click chemistry has been demonstrated as an effective method to incorporate bulky and complex molecules to a variety of surfaces [2-6]. This route has introduced numerous possibilities of tailoring molecular surfaces.

Here, we have employed a Cu-catalyzed azide-alkyne cycloaddition (CuAAC) click reaction to attach Ru<sub>2</sub>(ap)<sub>4</sub>-(C≡C-C<sub>6</sub>H<sub>4</sub>-C≡CH), (henceforth referred to as Ru<sub>2</sub>-alkynyl) to Au and SiO<sub>2</sub> surfaces. First, we form an azide-terminated monolayer on Au and SiO<sub>2</sub> by using azidoundecanethiol and azidoundecyl trimethoxysilane, respectively. Next, the Ru<sub>2</sub>-alkynyl is linked to the azide-containing monolayers via a CuAAC reaction (adapted from Ref. 4). The clicked-on Ru<sub>2</sub>-alkynyl molecule was physically characterized by X-ray photoelectron spectroscopy (XPS) and infrared (IR) spectroscopy. The formation of the azide monolayer on Au

and SiO<sub>2</sub> surfaces is confirmed by IR measurements. After the CuAAC click reaction of the Ru<sub>2</sub>-alkynyl to the azide-treated surfaces, there is a reduction of the azide stretch in the IR which indirectly confirms the progress of the click reaction. The incorporation of Ru<sub>2</sub>-alkynyl is confirmed by XPS, where we estimate the Ru<sub>2</sub>-alkynyl covers about 10% of the azide sites.

The formation of molecular electronic junctions (Au/Ru<sub>2</sub>-alkynyl/Si structures) by flip-chip lamination [7] for electrical and backside IR [8] characterizations is currently ongoing. With these results, we are able to obtain a thorough picture linking electrical properties with physical and chemical structure of the diruthenium molecular junctions.

S. P. Cummings et al., *Organometallics* 29, (2010) 2783 – 2788.

R. Chelmoski et al., *Langmuir* 25, (2009) 11480-11485.

G. Qin et al., *J. Am. Chem. Soc.* 132, (2010) 16432-16441.

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A. C. Cardiel et al., *ACS Nano* 6, (2012) 310-318.

P. K. B. Palomaki and P. H. Dinolfo, *Langmuir* 26, (2010) 9677 – 9685.

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C. A. Richter et al., *J. Phys. Chem. B* 109, (2005) 21836 - 21841.

#### 4:00pm **TF+EM+SS-ThA7 Vapor Phase Surface Functionalization using Hybrid SAMs / ALD Heterostructures**, *L. Lecordier, M.J. Dalberth, G. Sundaram, J.S. Becker*, Cambridge Nanotech, Inc.

Self-assembled monolayers and atomic layer deposition are two methodologies commonly used to tailor surface properties at the atomic scale and achieve thin films with excellent electrical, chemical, mechanical or optical performances thus leading to a broad portfolio of applications from thin films for flexible electronics to biological surface functionalization.

While ALD film growth is the result of a discretized process where inorganic monolayers are built upon one another through a sequence of reactant exposure/purge cycles until the desired film thickness is achieved (typically 1-100nm), SAMs on the other hand allow the deposition of a single ordered organic monolayer. Both processes are driven by self-limited chemisorbed surface reactions and can be deposited under vacuum conditions at relatively low temperatures, facilitating the integration of these two processes on a single platform.

The current work was implemented on a commercial Cambridge Nanotech hybrid ALD/SAMs platform. The tool is based on a Savannah S200 ALD reactor and integrates a SAMs kit for the accurate delivery of a variety of SAMs reactants. Stable SAMs monolayers are deposited under vacuum conditions using exposure mode (EXPO) characteristic of Cambridge Nanotech ALD tools. Key process metrics such as precursor pulse and exposure times, source and reactor temperatures were investigated for a variety of precursors including non-polar hydrophobic alkylsilanes (DTS), oleophobic fluorinated silanes (FOTS), hydrophilic polyethylene glycol (PEG) and thiols. In all cases, the self-limited surface saturation was achieved within 1 to 15 min minute exposures to the precursor at temperature ranging from 50 to 110°C.

In some instances, oxide ALD films were used to deposit a very thin seed layers (<5Å) to promote the adhesion of a SAM without prior surface cleaning/conditioning. Heterostructures based on oxide ALD (Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, SiO<sub>2</sub>) and SAMs were also obtained to develop efficient water moisture barriers to be used for encapsulation. Overall the integration of these processes in a single platform provides a versatile and scalable method to surface functionalization where surface properties such as wettability can be tuned by controlling at the atomic level the structures of these hybrid coatings.

#### 4:20pm **TF+EM+SS-ThA8 Chemically and Mechanically Stable Hydrophobic Thin Films Prepared by Combination of Layer-By-Layer Approach and Thiolene Chemistry**, *N. Madaan, J.A. Tuscano, N.R. Romriell, M.R. Linford*, Brigham Young University

The current aim of our research is to create robust hydrophobic thin films, for glass/silicon substrates, which can withstand extreme pH conditions and temperatures, have good release properties, and at the same time are mechanically durable. This approach consists of deposition of 3-aminopropyltriethoxy silane (APTES) on a silicon substrate followed by layer-by-layer deposition and cross-linking of alternating layers of poly(acrylic acid) (PAA) and poly(allylamine hydrochloride) (PAH). These nylon-like cross-linked layers have already been demonstrated to possess stability in extreme pH conditions. Their permeability can be controlled by the extent of crosslinking, which depends on the time and temperature of crosslinking. A careful study using X-ray photoelectron spectroscopy in our lab showed 71% cross-linking when these assemblies were heated at 250 °C for 2 h. We also found that the ratio of ammonium to amine groups in these

bilayers is 2:1, and that there is a potential to impart additional properties to the films by utilizing these residual amine groups. This was part of an experimental design over a series of times and temperatures. These substrates can further be modified using a variety of chemistries. One approach is to expose these substrates to basic NaOH solution (pH ~ 10) in order to deprotonate the ammonium groups of the terminal PAH layer followed by treatment with Traut's reagent to convert amine groups into thiol groups. The thiol groups are then reacted with 1,2-polybutadiene and a perfluoroalkane thiol using thiol-ene chemistry. Another approach is to use hydrolyzed poly(maleic anhydride alt 1-octadecene) as a terminal electrostatic anionic layer. A chemical and tribological stability comparison will be performed between the above prepared films and a perfluoroalkane silane film on Si substrates. The effect of the total thickness of cross-linked PAH-PAA bilayers on the stability of prepared films will be studied. The substrates are thoroughly analyzed at each surface modification step using X-ray photoelectron spectroscopy, time-of-flight secondary ion mass spectrometry, ellipsometry, water contact angles, and atomic force microscopy.

#### 4:40pm **TF+EM+SS-ThA9 A Detailed Investigation of the Conditions for Monolayer Deposition from Silane Precursors**, *J. Knauf*, Advanced Molecular Films GmbH / RWTH Aachen University, Germany, *L. Reddemann*, Advanced Molecular Films GmbH / Universität zu Köln, Germany, *A. Böker*, RWTH Aachen University, Germany, *K. Reihls*, Advanced Molecular Films GmbH, Germany

We have systematically investigated the process parameters for the vapor-phase deposition of monolayers from fluoroalkylated silane precursors. Our study reveals the influence of many process parameters on the molecular structure of the monolayers. Of particular interest to us are wetting and frictional properties of the monolayer obtained from the variation of process conditions. For reproducibly preparing high quality films particular parameters have to be meticulously controlled in a very narrow range which is not achievable without advanced deposition equipment.

Although the deposition of monolayers from silane precursors has been accomplished by various methods and has been subject to numerous studies, the properties and reproducibility of the resulting films remain unsatisfying for many applications. As an example, fluid wall slippage strongly depends on small changes in monolayer processing conditions which sensitively influence the structure of the monolayer deposited on structured surfaces [1].

Self-assembled monolayers (SAMs) were prepared by controlling a variety of process parameters, such as processing sequence and partial pressures of reactive compounds, deposition temperatures, adsorption/desorption times. These conditions were investigated for linear fluoroalkylated silane precursors of different chain lengths.

SAMs were deposited from fluoroalkylated silane precursors on pre-treated Si-wafers. Samples were examined by dynamic contact angle measurements, x-ray photoelectron spectroscopy (XPS), and static secondary ion mass spectrometry (sSIMS). The precursors applied were linear *1H,1H,2H,2H*-Perfluoroalkyltrichlorosilanes and varying chain lengths of the fluoroalkyl part were used for comparative studies based on detailed investigations using *1H,1H,2H,2H*-Perfluorododecyltrichlorosilane. Short-chain precursors were commercially available in ready-to-use quality whereas longer-chain compounds starting from *1H,1H,2H,2H*-Perfluorododecyltrichlorosilane were synthesized in our labs. While the short-chain compounds could be processed by routine measures special precautions had to be applied for storage and handling of longer-chain compounds due to their higher reactivity.

Results of the study of deposition conditions will be presented and discussed and may serve as a guideline for the reproducible preparation of well-defined monolayers from silane precursors.

[1] L. Reddemann, J. Knauf, A. Böker, K. Reihls, 14th International Conference on Organized Molecular Films (ICOMF14) - LB14, Abstract 146 (2012)

#### 5:00pm **TF+EM+SS-ThA10 Self Limiting Behavior in the Directed Self-Assembly of Mounds on Patterned GaAs(001)**, *C.-F. Lin*, University of Maryland, *C.J.K. Richardson*, Laboratory for Physical Science, *H.-C. Kan*, University of Maryland, *N.C. Bartelt*, Sandia National Laboratories, *R.J. Phaneuf*, University of Maryland

We present results demonstrating directed self assembly of nm scale mounds during molecular beam epitaxial growth on patterned GaAs(001)

surfaces. In the initial stages of growth, a lithographically-defined pattern directs the spontaneous formation of multilayer islands at the centers of bridges between near-neighbor nanopits along [110] crystal orientation, seemingly due to the presence of an Ehrlich-Schwoebel barrier. As growth continues, the heights of mounds at these 2-fold bridge sites "self-limit". Beyond this point mounds at other, 4-fold bridge sites dominate the topography, but these self-limit as well. This behavior suggests the existence of a minimum, 'critical terrace width' for nucleation of islands during growth, and provides a physical mechanism for understanding the transient nature of the observed instability during growth on these patterned surfaces

5:20pm **TF+EM+SS-ThA11 Characterization of Fully Functional Spray-on Antibody Thin Film**, *J.J. Figueroa, S. Magana, D. Lim, R. Schlaf*, University of South Florida

Physical adsorption (solid-liquid interface) is known as a simple and rapid option to immobilize biomolecules on various surfaces. Proteins, receptors and antibodies are attached via physisorption to different surfaces by various attachment protocols. However, physical adsorption has been often labeled in the past with disadvantages like variability, reversibility and low surface density of immobilized biomolecules. In contrast, the presented research demonstrates that spray deposition with a pneumatic nebulizer can be used to immobilize fully functional and stable physisorbed antibody coatings on glass surfaces with high reproducibility.

The experiments were performed using a low flow concentric nebulizer (commonly used on mass spectrometry), regular glass slides as a substrate and *E. coli* O157:H7 antibody as prototypical test system. The antibody films were examined for functionality, specificity and shelf life. A series of films with varying thickness and deposition conditions was characterized with respect to functionality, mechanical stability, surface morphology and antibody density. The results demonstrate that the films are comparable to films prepared with the standard covalent attachment protocol (avidin-biotin). They show low denaturation or conformational changes, minimal loss during the rinsing process suggesting good attachment to the surface, and they perform as well with regard to sensitivity, specificity and shelf-life. The morphology studies suggest that the non-oriented attachment of the spray deposited antibodies (compared to the oriented attachment achieved with the covalent attachment scheme) is compensated by a higher antibody density enabled by the non-equilibrium spray deposition process.

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