

# Wednesday Morning, October 31, 2012

## Electronic Materials and Processing

Room: 9 - Session EM+TF-WeM

### Hybrid Electronic Materials and Interfaces

**Moderator:** M.R. Linford, Brigham Young University, A.J. Muscat, University of Arizona

8:00am **EM+TF-WeM1 Versatile Electron Beam Chemical Lithography on the Basis of Monomolecular Films, M. Zharnikov, University of Heidelberg, Germany** **INVITED**

The talk reviews recent progress in Electron Beam Chemical Lithography (EBCL) on the basis of monomolecular templates provided by self-assembled monolayers (SAMs). Due to the monolayer thickness of SAMs and molecular size of their structural building blocks, patterning down to few nanometers is in principle possible. Depending on the architecture of the SAM constituents, different EBCL strategies can be used [1]. In the case of aromatic backbone, selective modification of specific tail groups at the SAM-ambient interface can be exploited [1]. In the case of aliphatic backbone, irradiation-promoted exchange reaction between the molecules in the primary SAM and potential molecular substituents can be used [2]. A further promising technique within the EBCL framework is Electron Beam Activation Lithography which involves activation of the amino tail groups of the primary SAM template disabled by specific quencher moieties [3]. This method is especially useful for the fabrication of morphological patterns. EBCL can also be adapted for biological applications, based on protein-repelling templates [4]. One can either perform a direct writing in such a template, which can be both SAM-based and polymer-like, or apply irradiation-promoted exchange reaction with well-controlled parameters. Using the above techniques, chemical patterning and surface engineering on the length scale ranging from cm to nm can be performed. Not only simple dot or stripe structures, but complex gradient-like and biology-inspired patterns can be fabricated as will be demonstrated by representative examples.

[1] M. Zharnikov and M. Grunze, *J. Vac. Sci. Technol. B* **20**, 1793-1807 (2002).

[2] N. Ballav, S. Schilp, and M. Zharnikov, *Angew. Chem. Int. Ed.* **47**, 1421-1424 (2008).

[3] S. Schilp, N. Ballav, and M. Zharnikov, *Angew. Chem. Int. Ed.* **47**, 6786-6789 (2008).

[4] N. Ballav, H. Thomas, T. Winkler, A. Terfort, and M. Zharnikov, *Angew. Chem. Int. Ed.* **48**, 5833-5836 (2009); *Nature*, **460**, 308 (2009).

8:40am **EM+TF-WeM3 Covalently Linked Organic Monolayers on Silicon Surfaces: Making Them Better, Stronger, Faster!, H. Zuithof, Wageningen University, Netherlands**

Covalently linked organic monolayers on silicon surfaces provide a prime example of hybrid electronic materials. Such systems are required on the one hand to passivate the Si surface, and on the other hand provide an optimal electrical link between the bulk of the Si semiconductor and the liquid with which it interacts.

To obtain an optimal passivation a highly dense monolayer is required, and we present novel agents and methods that yield a denser formation of the monolayers. At the same time monolayer formation can be made faster, which reduces the chance for competing silicon oxide formation. Finally, this combination of properties is desired for really thin monolayers, which drives research to allow attachment of small molecules. The paper will present a combination of such newly developed methods, properties of the resulting monolayers and an approach for further systematic improvements.

9:00am **EM+TF-WeM4 Probing the Intrinsic Organic/Semiconductor Interface, W. Peng, O. Seitz, R. Chapman, University of Texas at Dallas, E.M. Vogel, Georgia Institute of Technology, Y.J. Chabal, University of Texas at Dallas**

The electronic properties of organic/semiconductor interfaces are crucial for a variety of applications, such as organic dielectrics and organic/inorganic hybrid solar cells. However, the accurate characterization of these interfaces is prevented by the large tunneling current through the molecular layer. Moreover, standard fabrication methods, such as the formation of top metal contact via evaporation, cause damages during the processing even if applied directly with extreme caution. We present here a novel method to protect the interface with a layer of high- $\kappa$  dielectric ( $\text{Al}_2\text{O}_3$ ) gently deposited on top of the organic layer using atomic layer deposition. The metal precursor reacts with the carboxylic head group of the self-assembled

monolayer (SAM) layer without affecting the underlying SAM/Si interface. Due to the increase of the dielectric layer thickness ( $\text{SAM}+\text{Al}_2\text{O}_3$ ), a large reduction in tunneling leakage current occurs, and conductance voltage measurements can be implemented with a mercury probe setup. Moreover, the gate stack shows enough robustness to survive the entire MOS capacitor fabrication. Capacitance voltage measurements show small frequency dispersion and a low  $D_{it}$ , on the order of  $10^{11} \text{ cm}^{-2}\text{eV}^{-1}$ , for the intrinsic SAM/Si interface demonstrating inherent high quality when it is protected by the  $\text{Al}_2\text{O}_3$  layer.

9:20am **EM+TF-WeM5 Towards Organic Electronics: Methods for the Selective Deposition of Semiconductors and Metals, J. Yang, Z. Shi, K. Borner, A.V. Walker, University of Texas at Dallas**

We describe recent progress in our laboratories to build robust complex two- and three-dimensional molecular constructs. This work has important applications in photovoltaics, molecular and organic electronics, sensing, photonics and other technologies. Several recent developments are discussed including the chemical bath deposition of PbS, the UV photoassisted chemical vapor deposition of Al, and the formation of Ni and Cu nanowires on micron-scale patterned surfaces. Optimization and further development of these techniques requires a detailed understanding of the reaction pathways involved in the interaction of organic thin films with metals, organometallic compounds, ions, and other compounds.

9:40am **EM+TF-WeM6 Electroless Deposition of Co on  $\text{SiO}_2$  Surfaces Modified by an Aminosilane Self-Assembled Monolayer, R. Jain, A. Ng, E. White, A.J. Muscat, University of Arizona**

As device interconnects continue to shrink in size, the formation of diffusion barriers between dielectric and metal surfaces becomes more difficult. Self-assembled monolayers (SAMs) can be used to chemically activate a variety of surfaces, and their potential for uniform and defect-free monolayer formation makes them attractive alternatives for barrier layers. SAMs can also serve as adhesion layers to promote the electroless deposition (ELD) of metals on some dielectric surfaces. A 3-aminopropyltrimethoxysilane (APTMS) SAM was formed on a well-hydroxylated  $\text{SiO}_2$  surface and studied as a function of solvent (methanol, IPA, and toluene), APTMS concentration (5.72 mM and 57.2 mM), and post-deposition rinsing in methanol, IPA or chloroform depending on the solvent used. An aminopropylsilane monolayer with a thickness of  $7.8 \pm 0.2 \text{ \AA}$  and roughness of  $3 \pm 1 \text{ \AA}$  was formed at an APTMS concentration of 5.72 mM in methanol and IPA, but multilayers were formed in toluene, which were deposited at a rate of  $0.4 \pm 0.06 \text{ \AA/min}$  and roughness of  $31 \pm 18 \text{ \AA}$ . The N 1s XPS peak at a binding energy (BE) of 398.8 eV verified that a primary amine group ( $-\text{NH}_2$ ) was present together with an equal coverage of protonated amine ( $-\text{NH}_3^+$ ). Based on N 1s XPS peak areas, the molecular density of the aminopropylsilane monolayer was  $4.2 \pm 0.6 \text{ molecules/nm}^2$ , which is about equal to the accepted value of the OH group density on the Si surface. ELD processes are known to be sensitive to surface termination and require a metal catalyst, such as palladium, to activate the surface. A layer of Pd atoms was deposited by immersing the APTMS SAM surfaces in an 80 mM  $\text{PdCl}_2\text{-HCl}$  solution for 2 min, yielding one Pd atom bonded to two amine groups based on XPS peak areas. These results suggest that Pd atoms are bonded to primary amines rather than protonated amines resulting in a coverage of half of the N sites. Cobalt was plated by immersing the Pd-coated surface in a solution of 0.05 M  $\text{CoSO}_4$ , 0.2 M dimethylaminoborane (DMAB), and 0.01 M diethylenetriamine (DETA). Cobalt replaced the Pd atoms on the surface depositing a seed layer that auto-catalytically yielded a thick cobalt film on the surface. The thickness of the Co increased with the deposition time as verified by both the Co 2p peak at a BE of 777.2 eV and attenuation of the Si 2p peak with time. These results demonstrate that an aminopropyl silane adhesion layer binds metals such as Co. The next step is to test the effectiveness as a diffusion barrier.

10:40am **EM+TF-WeM9 Polymer-Colloidal Nanocrystal Hybrid Materials for Photovoltaic Applications, J. Xue, R. Zhou, P.H. Holloway, University of Florida** **INVITED**

Hybrid photovoltaic (PV) cells based on conjugated polymers and colloidal inorganic semiconductor nanoparticles have attracted significant attention as an alternative for all-organic solar cells. However, so far the highest efficiencies for hybrid PV cells have been limited to 2-3%, significantly lower than that of all-organic PV cells. One main reason for the lower performance is attributed to the complex interfaces and surfaces involving the inorganic nanocrystals.

Here we report our recent work that significantly improves the efficiency of hybrid PV cells to the 5% level. First, a 30-70% increase in the device efficiency was achieved by incorporating a solution-processed ZnO nanoparticle layer between the active layer and the cathode. This was

attributed to a combination of electronic, optical, chemical, and morphological effects, including blocking leakage of photogenerated holes to the cathode, optimizing the optical intensity profile in the hybrid active layer, minimizing recombination or quenching of photogenerated excitons and charge carriers. Maximum power conversion efficiencies of 2.5% and 3.5% were achieved with a high-gap polymer P3HT and a low-gap polymer PCPDTBT, respectively. The incorporation of the ZnO nanoparticle layer also drastically improves the stability of the hybrid PV cells.

We further demonstrated another 30-50% improvement in the efficiencies of hybrid PV cells by treating the hybrid active layer in an acetonitrile solution with 1% ethanedithiol (EDT). This leads to a maximum efficiency of ~5.0% for the EDT-treated hybrid PV cell with a PCPDTBT:CdSe nanorod active layer. Detailed characterizations of the hybrid active layers before and after the EDT treatment revealed no appreciable differences in their morphology and absorption spectra; however the phosphonic acid organic ligands on CdSe nanocrystals are more completely removed, and an improved electron mobility was obtained upon EDT treatment. We attribute the enhanced efficiency to more complete removal of exciton/charge recombination centers and the subsequent atomic layer passivation of the CdSe nanorod surface.

11:20am **EM+TF-WeM11** **Obtention of Deterministic Patterns through Wrinkling Formation**, *J.L. Yague, J. Yin, D. Eggenstele, M.C. Boyce, K.K. Gleason*, Massachusetts Institute of Technology

Formation of wrinkles through buckling of a stiff coating on a compliant substrate can be found very commonly in nature. For instance, the epidermal ridges, which form our fingerprints, show a very unique pattern due to out-of-plane bending of the epidermis. The use of wrinkling to obtain patterned surfaces has become increasingly significant for a wide range of applications, such as: microfluidic, tunable wettability, stretchable electronics, photonics or anti-fouling surfaces. In this work, we demonstrate the ability to obtain labyrinth and herringbone patterns using a 2D stretching-releasing approach.

On top of a compliant substrate, an acrylate-based polymer is deposited by initiated chemical vapor deposition (iCVD). iCVD is a solvent-free method that yields a conformal thin coating on virtually any substrate, giving a controllable thickness and tunable structural, mechanical, thermal, wetting, and swelling properties. Monomer together with an initiator is introduced into a reactor chamber under vacuum, where the initiator is decomposed over resistively heated filaments to obtain radicals. Radicals and monomer are then adsorbed on a surface, which is kept at a controlled temperature to promote adsorption, to yield the polymer by the classical free-radical mechanism. Here, deterministic herringbone patterns are achieved through wrinkling of the polymer thin film. Furthermore, a simplified theoretical model is developed to predict the geometry of the ordered herringbone pattern. Depending on the experimental conditions is possible to control the features of such pattern. We report, for first time, the obtention of herringbone patterns with a jog angle lower than 90°. Finally, this method also provides a tool to determine the Young's modulus of the films based only on the characteristic wavelengths of the pattern.

11:40am **EM+TF-WeM12** **Surface Dynamics of Hybrid Silicon Interfaces Explored via Helium Atom Scattering**, *Z.M. Hund, R.D. Brown*, University of Chicago, *L.E. O'Leary*, California Institute of Technology, *D. Campi, M. Bernasconi, G. Benedek*, Università di Milano-Bicocca, Italy, *N.S. Lewis*, California Institute of Technology, *S.J. Sibener*, University of Chicago

Surface dynamical properties of methyl-terminated silicon(111) were investigated with energy and momentum resolved inelastic helium atom scattering measurements. The narrow energy distribution and nondestructive nature of neutral helium atom beams allow us to probe the vibrational dynamics of this hybrid organic-semiconductor interface. Time-of-flight experiments identify single phonon inelastic scattering events including, but not limited to, those attributed to Rayleigh wave excitations. We have mapped out the entire surface Brillouin zone along the nearest neighbor and next nearest neighbor azimuths,  $\langle 011 \rangle$  and  $\langle 121 \rangle$ , respectively. Our experimental results are in excellent agreement with density functional perturbation theory calculations, which provide a detailed description of the dispersion curves. The combination of experimental measurements with theoretical calculations allows us to determine the interfacial Si-Si force constants, including coupling between the molecular adlayer and the substrate, displacement fields, and mode polarizations. Helium atom scattering complemented with DFPT calculations allow us to quantify these effects. Additionally, isotopic effects were probed by mapping the dispersion curves for the perdeutero-methylated silicon surface. Our results will be discussed with respect to hydrogen-terminated Si(111).

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