Thursday Afternoon, November 10, 2016

Thin Film
Room 105A - Session TF-ThA

Self-assembled Monolayers and Organic/Inorganic Interface Engineering

Moderators: Matthew Linford, Brigham Young University, Adrienne Stiff-Roberts, Duke University

2:20pm **TF-ThA1 Surface Affinity Control by Polymer Brushes for Direct Self-Assembly**, *R. Tiron, A. Gharbi,* ***M. Argoud****, F. Delachat, P. Pimenta Barros,* CEA-LETI, MINATEC, France*; X. Chevalier,* ARKEMA FRANCE*; S. Bouanani,* STMicroelectronics, France*; G. Claveau, C. Lapeyre,* CEA-LETI, MINATEC*; G. Chamiot-Maitrala,* CEA-LETI, France*; C. Monget, V. Farys,* STMicroelectronics, France*; C. Nicolet, C. Navarro,* ARKEMA FRANCE **INVITED**

The ongoing progress in nanoscience and nanotechnology leads to a continual device miniaturization. Until now, lithography has been the main driving force of this process. Block copolymers have become of great interest for high-resolution patterning due to their low fabrication cost, ease of use and high throughput potential. Self-assembling materials used in conjunction with the most advanced exposure tools may extend the current manufacturing practices to dimensions of 10nm and beyond. Density multiplication of patterned templates by DSA of block copolymers stands out as a promising alternative to overcome the limitation of conventional lithography.

In this paper, we investigate the potential of DSA to address both contact via level patterning as well as line and space application. Using the 300mm pilot line available in LETI and Arkema materials, our approach is based on the graphoepitaxy of PS-b-PMMA block copolymers. Our integration scheme is based on BCP self-assembly inside organic hard mask guiding patterns obtained using 193i nm lithography. The process is monitored at different steps: the generation of guiding patterns, the directed self-assembly of block copolymers and PMMA removal, and finally the transfer of PS patterns into the metallic under layer by plasma etching.

Furthermore, several process flows are investigated, either by tuning different material related parameters such as the block copolymer intrinsic period or the interaction with the guiding pattern surface (sidewall and bottom-side affinity). The final lithographic performances are finely optimized as a function of the self-assembly process parameters such as the film thickness and bake (temperature and time).

Finally, DSA performances as a function of guiding patterns density are investigated. Thus, for the best integration approach, defect-free isolated and dense patterns for both contact shrink and multiplication (doubling and more) have been achieved on the same processed wafer.

These results show that contact hole shrink and multiplication approach using DSA is well compatible with the conventional integration used for CMOS technology.

3:00pm **TF-ThA3 Measuring the Rate of Organic Reactions on Surfaces**, ***Rickdeb Sen****, J. Escorihuela, M.M.J. Smulders, H. Zuilhof,* Wageningen University, Netherlands

Ultrathin coatings like self-assembled monolayers and polymer brushes have been used for a wide variety of studies and applications. Reactions within such monolayers or brushes are often difficult to follow, and their rates are typically not measurable: apart from a handful of cases in which electrochemical methods have been used, no rigorously measured kinetics on reactions within e.g. self-assembled monolayers are available.

The current presentation will outline a generic approach, combining ambient mass spectrometry and XPS, to fill this gap, and provide a novel method to measure the rate of intramonolayer or intrapolymer organic reactions. Examples will include a variety of so-called click reactions, as these display a very high potential in materials science.

Reference: Langmuir 2016, 32, 3412–3419

4:00pm **TF-ThA6 *Operando* Investigation of Chemical Bonding at Hybrid Interfaces: the Effect of Humidity on Polymer/metal Oxide Bonds**, ***Sven Pletincx****,* Vrije Universiteit Brussel, Belgium*; L. Trotochaud, A.R. Head, O. Karslıoğlu,* Lawrence Berkeley Lab, University of California, Berkeley*; L.I. Fockaert, J.M.C. Mol,* TU Delft, Netherlands*; H. Bluhm,* Lawrence Berkeley Lab, University of California, Berkeley*; H. Terryn, T. Hauffman,* Vrije Universiteit Brussel, Belgium

Stability in aqueous and corrosive environments of formed bonds between carboxylic acid functional groups of a polymer and a hydroxylated surface of aluminium oxide has a great relevance to a broad range of applications. One of the most important industrial problems of adhesion phenomena includes the loss of desired chemical interactions at the interface as a result of humidity and ionic compounds present in the atmosphere. Conventional vacuum techniques do not permit analysis under atmospheric conditions or can nullify the influence of ex-situ atmospheric modifications upon exposure of the sample to an ultra-high vacuum environment. Also, because of the relatively thick polymer layer present in conventional hybrid systems, a buried interface exists, which is difficult to characterize with surface-sensitive analytical techniques. Recent developments in the field of ambient-pressure x-ray photoelectron spectroscopy (APXPS) enable a novel approach to probe these interfaces. A broad range of relative humidities can be reached in the analysis chamber, making it possible to unravel interfacial chemistry changes *operando*.

The amount of bonds formed at the hybrid interface and their binding mechanism (monodentate, bidentate, Brønsted interactions, Lewis interactions) are largely determined by oxide properties such as surface hydroxyl content, acid/base character, and dielectric properties. In this work, aluminium oxide is synthesized by electropolishing and anodizing pretreatment steps to carefully control oxide properties on the nanoscale and fully characterized by different analysis techniques. Polyacrylic acid coatings are made sufficiently thin to access the interface with surface analysis techniques with probing depths between 5-10 nm.

Complementary to APXPS, a vibrational spectroscopy technique using the so-called Kretschmann configuration is used to characterize the formed bonds at the metal oxide/polymer interface. An Al layer is sputtered on an IR transparent crystal, with the Al thickness selected such that the FTIR signal from the oxide/polymer interface is amplified as a result of the Kretschmann effect, and thus an interface-specific spectrum of the oxide/polymer surface is attained. This way, we have direct access to the interface, and the influence of an above-the-polymer electrolyte (i.e. H_2O) can be probed. Preliminary results show an increase in the amount of bonds at the oxide/polymer interface, together with an increase in water content directly at this interface. It seems that water, at least during the first 24 hours of interaction, triggers an increased wet adhesion.

4:20pm **TF-ThA7 Integration of Redox-Active Diruthenium-based Molecular Layer onto Electrodes for Memory Device Applications**, ***Sujitra Pookpanratana****,* National Institute of Standards and Technology (NIST)*; H. Zhu,* George Mason University*; J.W.F. Robertson,* NIST*; S.N. Natoli,* Purdue University*; E.G. Bittle, C.A. Richter,* NIST*; T. Ren,* Purdue University*; Q. Li,* George Mason University*; C.A. Hacker,* NIST

Attaching and integrating electrochemically-active molecules to a variety of different surfaces is of importance for applications in catalysis, memory devices, and molecular electronics. With the increasing demand for personal electronics, growth in Flash-based memory has increased dramatically. However, the dimensional scaling of memory components faces many critical material limitations. A critical component to the memory device is the floating gate or charge trapping layer. To scale the charge trapping layer to nanometer dimensions, one approach is to use a discrete charge storage layer that is based on organic molecules.[1,2,3] Reduction-oxidation (redox) active organic molecules hold potential for memory devices due to their nanoscale dimensions, potential for high charge density, and synthetic flexibility that could be tailor-made for specific electronic functionality.

Here, we investigated the potential of diruthenium-bearing organometallic molecules as the charge trapping layer for memory devices. Diruthenium-bearing organometallic molecules display multiple redox states,[4] which makes them ideal to incorporate within non-volatile memory devices. Monolayer assembly is performed in a stepwise fashion by first forming azide-terminated monolayer on SiO_2 by using azidoundecyl trimethoxysilane followed by a Cu-catalyzed azide-alkyne cycloaddition click reaction to attach diruthenium (Ru_2) compounds (note: SiO_2 serves as the tunneling layer).[5] Infrared spectroscopy and X-ray photoelectron spectroscopy confirmed the Ru_2 attachment. Ultraviolet photoelectron spectroscopy identified the occupied electronic levels of the hybrid organic-inorganic surfaces before and after click reaction. Voltammetric measurements on Ru_2-terminated SiO_2/Si and Au electrodes confirm that the Ru_2 is still electrochemically-active with accessible electronic states integrated on both surfaces.

To complete the memory capacitor device, an Al_2O_3 layer (serving as a charge blocking layer) was deposited by atomic layer deposition over the molecular layer followed by a metal Pd gate. The impact of different Ru_2 compounds on the electronic structure and electrochemical properties of the electrodes and properties of the memory devices will be compared. Our results will provide future design considerations and limitations for molecular-integrated memory devices.

1. T. Shaw et al., IEEE T. Electron. Dev. **58** (3), 826-834 (2011).

2. D. Beckmeier and H. Baumgärtner, J. Appl. Phys. **113** (4), 044520 (2013).

3. H. Zhu, et al., Appl. Phys. Lett. **103** (5), - (2013).

4. W.-Z. Chen and T. Ren, Inorg. Chem. **45** (20), 8156-8164 (2006).

5. S. Pookpanratana, et al., Langmuir **30** (34), 10280-10289 (2014).

4:40pm **TF-ThA8 Fabrication Methods of Organic-Inorganic Hybrids Based on Atomic Layer Deposition***, Myung Mo Sung,* Hanyang University, Korea **INVITED**

Organic-inorganic hybrid materials are particularly attractive because they can provide means for not only combining the distinct properties of organic and inorganic components, but outperforming their constituents. The incorporation of inorganic layers into organic layers, therefore, provides the opportunity for developing new hybrid materials with synergic behavior, leading to improved performance. In this presentation, we report three fabrication methods of organic-inorganic hybrid materials using atomic layer deposition (ALD). (1) Molecular layer deposition (MLD) is a gas phase process analogous to ALD and also relies on sequential saturated surface reactions which result in the formation of a self-assembled organic monolayer in each sequence. The MLD method can be combined with ALD to take advantages of the possibility of obtaining organic–inorganic hybrid thin films. The advantages of the MLD technique combined with ALD include accurate control of film thickness, large-scale uniformity, excellent conformality, good reproducibility, multilayer processing capability, sharp interfaces, and excellent film qualities at relatively low temperatures. (2) Large-area graphene films produced by means of chemical vapor deposition (CVD) are polycrystalline and thus contain numerous grain boundaries that can greatly degrade their performance and produce inhomogeneous properties. A better grain boundary engineering in CVD graphene is essential to realize the full potential of graphene in large-scale applications. Here, we report a defect-selective atomic layer deposition (ALD) for stitching grain boundaries of CVD graphene with ZnO so as to increase the connectivity between grains. In the present ALD process, ZnO with hexagonal wurtzite structure was selectively grown mainly on the defect-rich grain boundaries to produce ZnO-stitched CVD graphene with well-connected grains. (3) ALD under high pressure showed that precursors often diffuse sub-surface into polymers. This subsurface diffusion and reaction cold result in the change of the chemical composition and the physical properties of the bulk polymers. Atomic layer infiltration provides a new approach for preparation of organic-inorganic hybrid materials from polymers.

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