

## Thin Films Division

Room: 20 - Session TF-FrM

### Self-assembled Monolayers and Organic/Inorganic Interface Engineering

Moderator: Adrienne Stiff-Roberts, Duke University

8:20am **TF-FrM1 Kinetics of Swelling and Deswelling in Thermoresponsive Polymers Deposited by Initiated Chemical Vapor Deposition**, *P. Salzmann*, Graz University of Technology, *A. Perrotta*, Eindhoven University of Technology, Netherlands, *AnnaMaria Coclite*, Graz University of Technology, Austria

Thermo-responsive polymers, like the Poly-(N Isopropylacrylamide) p(NIPAAm), change their properties (e.g. thickness and wettability) upon small changes in the environment temperature. This makes them suitable for interesting applications as smart sensors, artificial muscles or drug delivery systems. The change in the film properties arises from a coil to globule transition from a swollen hydrophilic state at temperatures below the lower critical solution temperature (LCST) to a shrunken hydrophobic state when the material is heated to temperatures higher than the LCST.

Cross-linked thin polymer films of NIPAAm were synthesized by initiated chemical vapor deposition (iCVD) and their thermoresponse was studied in situ in water and in humidity by ellipsometry.

The film thicknesses were up to three times higher at temperatures below the LCST than at higher temperatures. Temperature cycles and different heating ramps revealed different mechanism of swelling and deswelling. The response during the cooling (i.e. during the swelling) was characterized by an LCST of 23°C. During the heating process (i.e. deswelling) the LCST was as high as 36°C. Similar discrepancies were also observed with another thermoresponsive polymer (N,N-Diethylacrylamide) deposited by iCVD. The reason was ascribed to different diffusion kinetics of water in the polymer meshes, and different arrangements of the polymer chains at the interface with water, depending on the rate of increase or decrease in temperature. A detailed investigation of these processes will be shown due to its importance for sensing applications.

9:40am **TF-FrM5 the Curious Wetting Behavior of ALD Grown Al<sub>2</sub>O<sub>3</sub> Thin Film Surfaces**, *Yi Li, B.D. Piercy, M.D. Losego*, Georgia Institute of Technology

#### The curious wetting behavior of ALD grown Al<sub>2</sub>O<sub>3</sub> thin film surfaces

Yi Li, Brandon D. Piercy, Mark D. Losego

Conventional wisdom suggests that Al<sub>2</sub>O<sub>3</sub> surfaces should be hydrophilic. Recently, it was demonstrated by the Parsons lab at NC State that under certain conditions a few cycles of trimethylaluminum-water atomic layer deposition (ALD) transforms cotton fiber surfaces from hydrophilic to hydrophobic. These researchers suggest that adventitious carbon from ambient atmosphere is the source of this hydrophobicity, but they make no note of the universality of this phenomenon. In our effort to better understand this phenomenon, we discovered that ALD grown Al<sub>2</sub>O<sub>3</sub> thin films of “any” thickness (1 nm to >50 nm) on “any” substrate (including silicon) can be transformed into a relatively hydrophobic surface state (water contact angles > 80°) when heat treated under appropriate conditions. After heat treatment, ellipsometry detects several angstroms increase in thickness and XPS suggests this layer is some form of hydrocarbon. In this talk, we will discuss our evaluation of three hypotheses for the source of this hydrocarbon layer: (1) contamination from the heating environment (e.g., oven), (2) carbon contamination from the ALD deposition process (i.e., unpyrolyzed ligands), and (3) adventitious carbon from the atmosphere. To address hypotheses (1) and (3), Al<sub>2</sub>O<sub>3</sub> thin films grown by ALD to 10 nm thickness on silicon are found to become hydrophobic if we remove them from the ALD reactor and then re-anneal them in either a “dirty” ambient air oven or the “clean” ALD reactor under low-pressure and ultra-pure flowing nitrogen conditions. To further verify the purity of the ALD reactor, we have done this annealing step without breaking vacuum in the ALD reactor, leading to the Al<sub>2</sub>O<sub>3</sub> surface remaining hydrophilic. Films annealed to 700 °C for 4 hours to fully pyrolyzed any remaining organics (still hydrophilic) and then re-heated to 150 °C for 30 min are also found to turn hydrophobic, suggesting that residual carbon within the film is also not the source. Thus, we believe that the Al<sub>2</sub>O<sub>3</sub> surface is attracting adventitious carbon from ambient atmosphere and then reacting with the surface to form a hydrophobic layer. This reaction, which is thermally accelerated, appears to be key to the transition. We will report on how both temperature and time affect this surface reaction and our best understanding of the surface chemistry based on various surface spectroscopy techniques.

10:00am **TF-FrM6 Controlled Thicknesses of Vapor Deposited Silane Films**, *Brian Johnson, A. Diwan, M.R. Linford*, Brigham Young University  
Solution-based silane deposition is well known and has been widely studied. Increasingly, however, people are recognizing the importance of vapor phase deposition of these important reagents. Indeed, these gas phase depositions can be highly reproducible, they involve no solvent, and they can be integrated into production processes. Some of their disadvantages are the cost of the vacuum equipment/ovens needed, and the limitations inherent to the vapor phase, e.g., one cannot allow a polymerization of a silane to take place before the reagent/polymer is deposited on a surface as one can in a solution phase deposition. In this presentation we describe processes for controlling and increasing thicknesses of silane films on silicon surfaces. Variables studied in this work include process temperature, pressure, and reagent concentration. Silane films have been characterized by X-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (ToF-SIMS), spectroscopic ellipsometry (SE), and wetting. The depositions described in this work were performed in a commercial chemical vapor deposition (CVD) oven (the 1224P by Yield Engineering Systems). Special emphasis in these studies was placed on minimizing carryover between runs.

10:20am **TF-FrM7 Supramolecular Heterostructures formed by Sequential Epitaxial Deposition of Two-Dimensional Hydrogen-Bonded Arrays**, *V.V. Korolkov, M. Baldoni*, The University of Nottingham, UK, *K. Watanabe, T. Taniguchi*, National Institute for Materials Science, Japan, *E. Besley, Peter Beton*, The University of Nottingham, UK

The formation of two-dimensional supramolecular arrays provides a highly flexible route to the control of the spatial organization, down to the molecular scale, of the chemical functionality of a surface. These molecular networks, which can be formed through self-assembly processes on a variety of different substrates including semiconductors, metals, insulators<sup>9</sup> and layered materials, are, in almost all cases, limited to monolayer thickness. Progress towards the growth of higher layers has so far been much more limited, with demonstrations of bilayer growth and site-specific molecular adsorption. Specifically, the additional functional control, which may be achieved through the formation of heterostructures realized by placing one supramolecular layer on another and resulting in growth into the third dimension perpendicular to the substrate, has not been widely explored for these materials. Such additional control of material properties is well established for semiconductors, both organic and inorganic, and, more recently, layered materials, providing a strong motivation to explore analogue materials derived from stacked supramolecular networks. Here we describe the successful formation of heterostructures formed by the sequential growth of distinct one- and two-dimensional arrays. It is possible, using high resolution atomic force microscopy (AFM) to determine an epitaxial alignment between successive layers. Furthermore, we demonstrate using classical molecular dynamics (MD) simulations that the placement and dimensions of the layers may be robustly predicted using well established force-fields.

Supramolecular heterostructures<sup>1</sup> are formed by growing sequential layers of bi- and mono-component two-dimensional molecular arrays stabilized by hydrogen bonding. The heterostructures are formed on hexagonal boron nitride by depositing cyanuric acid/melamine (CA.M) followed by terephthalic acid (TPA) or trimesic acid (TMA) and imaged using atomic force microscopy under ambient conditions with resolution approaching 0.1 nm. A clear epitaxial arrangement is observed between these layers having intrinsically distinct symmetries and lattice constants, which for TMA/CA.M corresponds to a ( $\sqrt{3} \times \sqrt{3}$ )R30° phase, while TPA forms rows with a molecular separation that matches the CA.M period. Structures calculated using classical molecular dynamics are in excellent agreement with the orientation, registry and dimensions of the epitaxial layers. Calculations confirm that van der Waals interactions provide the dominant contribution to the adsorption energy and registry of the layers.

<sup>1</sup> Korolkov et al., Nat. Chem., 2017, in press.

10:40am **TF-FrM8 Functionalization and Stabilization of Ultrathin Alumina Films with Rhenium Photosensitizers**, *Wolf-Dietrich Zabka, D. Leuenberger*, Department of Physics, University of Zürich, Switzerland, *G. Mette*, University of Zürich, Switzerland, *C. Monney*, University of Zürich, Switzerland, *M. Mosberger*, University of Zürich, Switzerland, *B. Probst-Rüd*, University of Zürich, Switzerland, *R. Alberto, J. Osterwalder*, University of Zürich, Switzerland

Ultrathin (ut) oxide films with a thickness of few atomic layers are often used as model systems for oxide surfaces and their interaction with adatoms, particles and molecules. In particular, epitaxial ut-alumina films grown on NiAl alloys have been used to study a wide range of phenomena under UHV-

conditions [1,2]. However, their instability under ambient conditions limits the possibilities for application [3,4].

We developed a new wet chemistry setup directly attached to an existing ultra-high vacuum system that enables us to deposit self-assembled monolayers (SAM) from highly purified solvents onto substrates prepared under UHV conditions without exposure to air. The setup, the procedure for SAM-deposition and the characterization of residual contamination detected with X-ray photoelectron spectroscopy (XPS) will be described. Rhenium photosensitizers functionalized with carboxyl groups ( $\text{Re}(\text{CO})_3(\text{NCS})\text{bipy carb}$ ) are attached onto  $\text{Al}_2\text{O}_3$  films. XPS measurements indicate that the resulting structure is stable in air. First results from time-resolved photoemission spectroscopy suggest that by altering the oxide thickness, a variation of the lifetime of excited electrons can be achieved. Both, the substrate stabilization and the control of hot electron lifetimes offer new prospects for the application of such ultrathin oxide films involving charge transfer and related mechanisms.

[1] N. Nilius, Surf. Sci. Rep. 64, 595 (2009).

[2] U. Diebold, S. C. Li, and M. Schmid, Annu. Rev. Phys. Chem. 61, 129 (2010).

[3] A. Shavorskiy, K. Müller, J. T. Newberg, D. E. Starr, and H. Bluhm, J. Phys. Chem. C 118, 29340 (2014).

[4] J. Evertsson, F. Bertram, F. Zhang, L. Rullik, L. R. Merte, M. Shipilin, M. Soldemo, S. Ahmadi, N. Vinogradov, F. Carlà, J. Weissenrieder, M. Göthelid, J. Pan, A. Mikkelsen, J.-O. Nilsson, and E. Lundgren, Appl. Surf. Sci. 349, 826 (2015).

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