

Abstract No. efim444

Formation of Self-assembled Monolayers of Semifluorinated and Hydrocarbon Chlorosilanes on Silica from Liquid Carbon Dioxide

K. Efimenko, B. Novick, R. Carbonell, R. DeSimone, and J. Genzer (North Carolina State U.)

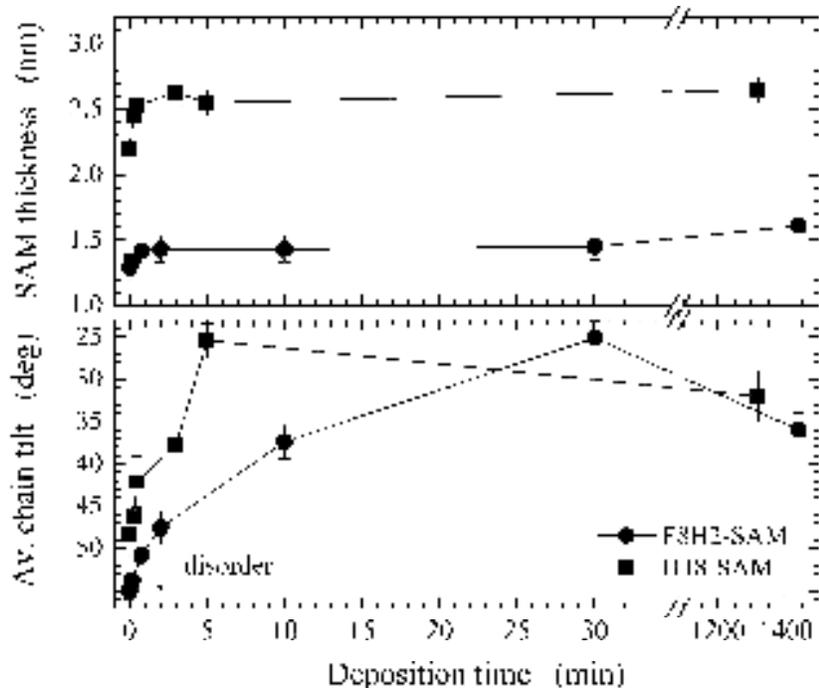
Beamline(s): U7A

Introduction: Thin polymeric films have long been recognized as important for tailoring the characteristics of materials surfaces. With recent advances in nanotechnology, calling for decreases in the feature sizes of nanodevices and microelectronic components to the nanometer scale, the need for a new class of interfacial modifiers with sizes comparable to the dimension of a single molecule becomes even more eminent. Such surfaces with nanometer thick and structurally well-defined surface modifiers can be prepared by depositing self-assembled monolayers (SAMs). Current techniques practiced to apply silane-based SAMs on materials surfaces involve either vapor- or liquid-phase depositions. We study the formation and properties of SAMs prepared by depositing semifluorinated and hydrocarbon chlorosilane precursors, $F(CF_2)_8(CH_2)_2SiCl_3$ (F8H2) and $H(CH_2)_{18}SiCl_3$ (H18), respectively, from vapor, organic solvent, and liquid CO_2 (l- CO_2). We use contact angle measurements and ellipsometry to follow the deposition kinetics of the molecules. NEXAFS is applied to monitor the orientation of the F8H2 and H18 molecules in their corresponding SAMs as a function of time.

Methods and Materials: Heptadecafluoro-1,1,2-tetrahydrodecyl trichlorosilane (F8H2) and n-octadecyl trichlorosilane (H18) were supplied by Gelest, Inc. and used as received. The SAM deposition was done either in: i) vapor, ii) organic liquid, and iii) l- CO_2 . A trace amount of water hydrolyzed the $-SiCl_3$ forming $-Si(OH)_3$ species, which then reacted with the hydroxyl groups on silica substrate and formed an organized SAM. The NEXAFS experiments were carried out on the NIST/Dow Soft X-ray Materials Characterization Facility at the National Synchrotron Light Source at Brookhaven National Laboratory (NSLS BNL). A measurement of the partial electron yield (PEY) intensity of NEXAFS spectral features allows for the identification of chemical bonds and determination of their relative population density within the sample. By collecting the PEY NEXAFS spectra at several θ ($20^\circ \leq \theta \leq 90^\circ$), where θ is the angle between the sample normal and the polarization vector of the x-ray beam, the surface molecular orientation of the SAM molecules on the silicon oxide surfaces can be determined.

Results: Contact angle measurements of the SAMs deposition kinetics reveal that regardless of the molecule type, the deposition rates from l- CO_2 exceed those from vapor or organic solvents by several orders of magnitude. We claim that this behavior is a consequence of i) a relatively high bulk concentration (l- CO_2 vs. vapor), and ii) higher solution diffusivity (l- CO_2 vs. organic solvent) of the silanes in l- CO_2 . Near-edge absorption fine structure (NEXAFS) is used to monitor the orientation of the F8H2 and H18 molecules in their corresponding SAMs as a function of time. Our NEXAFS data show that the F8H2 molecules adsorb initially from CO_2 without any molecular order in the monolayer. As more F8H2 molecules partition at the silicon oxide surface, they start to organize and orient. A complete monolayer order is achieved after ≈ 30 minutes exposure to F8H2/liquid CO_2 solutions. The deposition kinetics and molecular behavior of the H18 moieties in the SAMs is found to be different, however. Soon after washing the silica substrate with a H18/ CO_2 solution, the molecules adsorb and form an organized monolayer. Similar to the case of the semifluorinated species, the order in the H18-SAM increases with increasing time and saturates after ≈ 5 minutes exposure to H18/liquid CO_2 solution. We attribute the difference in the orientation kinetics to the different solubilities of F8H2 and H18 in CO_2 .

Acknowledgments: This work was supported by the NSF, The Camille & Henry Dreyfus Foundation, and the Kenan Center for the Utilization of CO_2 in Manufacturing. We thank Dr. Dan Fischer for his assistance during the course of the NEXAFS experiments.



(top) Ellipsometric thickness of F8H2-SAM (circles) and H18-SAM (squares) as a function of the deposition time from liquid CO₂ mixtures. The lines are guides to the eye.
 (bottom) Average tilt of the molecules in F8H2-SAM (circles) and H18-SAM (squares) as a function of the deposition time from liquid CO₂ mixtures as determined from the NEXAFS measurements. The lines are guides to the eye.