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Formation of Self-Assembled Monolayers with Liquid Carbon Dioxide

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Self-assembled monolayers (SAMs) are surface-grown materials with a thickness of a few billionths of a meter, and structurally well-defined physico-chemical characteristics. Scientists at North Carolina State University in Raleigh, and the University of North Carolina in Chapel Hill have studied the formation and properties of SAMs prepared by depositing organosilane molecules from their vapor phase or a liquid phase in which they are dissolved in an organic solvent or liquid carbon dioxide, thus exploring the possibility of replacing environmentally harmful vapor and organic solvents by liquid carbon dioxide.

Scientists can create thin films with sizes comparable to the dimension of a single molecule, which could be used in electronic components the size of a few nanometers, or billionths of a meter. Such nanometer-thick layers can be prepared by depositing self-assembled monolayers (SAMs) on a substrate.

Some of the most commonly used molecules forming SAMs are alkyls bearing either a mercapto [-SH] group or organosilanes that are terminated with a chlorosilane [-Si-Cl] or alkoxy silane [-Si-OR, R being either methyl or ethyl] moieties. Organosilanes are particularly useful for modifying the surfaces of silicon and other semiconductor surfaces that are covered with a nanometer-thick oxide layer, making them suitable for biosensors, the reduction of corrosion rates, pattern creation by lithographic processes, and friction reduction.

Current techniques involve either vapor- or liquid-phase deposition of organosilane-based SAMs on materials surfaces. The environmental impact of both vapor and liquid deposition processes and the rather slow deposition rates (hours

to days) call for exploring alternative media from which SAMs could be deposited. Compressed carbon dioxide (CO₂), either in the liquid or supercritical state (temperature of 31 degrees Celsius and pressure of 72 times the atmospheric pressure), is a benign solvent that should be considered as a viable substitute for current SAM deposition media.

We studied the formation and properties of SAMs based on semifluorinated and hydrocarbon trichlorosilane precursors, F(CF₂)₈(CH₂)₂SiCl₃ (F8H2) and H(CH₂)₁₈SiCl₃ (H18), respectively. The organosilanes were deposited onto flat silica surfaces either from



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their vapor phase or a liquid phase in which they are dissolved in an organic solvent or liquid CO₂ (**Figure 1**). To get insight into the formation mechanisms of the F8H2- and H18-SAMs, we determined the thickness, wetting characteristics, and the average tilt angle of the molecules on the surfaces.

The SAM thickness was measured by using a technique called ellipsometry, which uses polarized light to probe the dielectric (electric polarization) properties of the sample (**Figure 2**, top). The wettability of the SAM-covered substrates was determined by depositing various liquids on the SAMs and by measuring the angle between the SAM surface and the tangent to the liquid drop, called the contact angle. The ellipsometry and wettability results revealed that the primary mechanism controlling the SAM formation was the adsorption of the molecules to the surface and not the diffusion of the molecules to the substrate. We have also established that the SAM formation kinetics from CO₂ is slower than that from the vapor solvent, but faster when using an organic medium, and the overall SAM formation was shown to be fastest when

using CO₂ because of higher precursor concentrations.

We also studied the ordering kinetics of the F8H2 and H18 molecules in their corresponding SAMs by using near-edge x-ray absorption fine structure (NEXAFS) spectroscopy at the U7A beamline of the National Synchrotron Light Source. In NEXAFS spectroscopy, incoming x-rays are absorbed in the atoms of the material by exciting core electrons into unoccupied electronic states. In a given atom, an outer shell electron then occupies the core electronic state, and the energy released by this electron is transmitted to another electron that is ejected. By detecting these so-

called Auger electrons, we can determine the molecular orientation and the binding of the SAMs to the substrate's surface.

The NEXAFS results (**Figure 2**, bottom) revealed that F8H2 molecules deposited from liquid CO₂ initially adsorbed without any molecular order. As more F8H2 molecules are accumulated on the silicon oxide substrate, they started to organize and orient. A complete monolayer order was achieved after about 30 minutes. We found that the order in the H18 SAMs increased with increasing time, and that a complete order was achieved faster than with F8H2 SAMs, after about five minutes of exposure to

the H18 and liquid CO₂ solution.

We attribute the difference in the orientation kinetics to the different solubilities of F8H2 and H18 in liquid CO₂. While a higher solubility of the fluorinated part of the F8H2 molecule in liquid CO₂ slows down the complete monolayer organization, the high chemical incompatibility between the H18 molecules and liquid CO₂ leads to rapid reorientation of the H18 SAMs on the substrate. Also, possible intermolecular interactions between neighboring F8H2 chains may also be responsible for the slower organization kinetics in the F8H2 SAM.

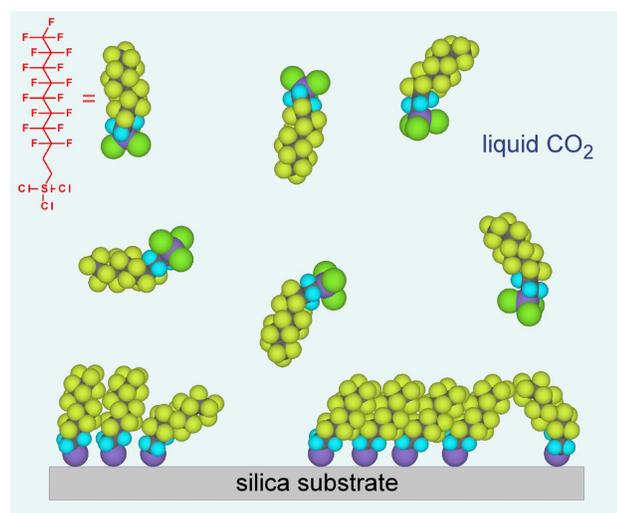


Figure 1. Schematic representation of the way semifluorinated trichlorosilanes (CF₂)₈(CH₂)₂SiCl₃ (F8H2) diluted in liquid carbon dioxide (CO₂) self-assemble onto a flat silica substrate. The precursor molecules react with a trace amount of moisture, thus giving up three chlorine atoms (green spheres) that make hydrogen chloride (HCl) molecules, forming (CF₂)₈(CH₂)₂Si(OH)₃, which self-organize on the substrate and bind to the surface's hydroxyl groups via a condensation reaction.

Figure 2. Thickness (top) and average tilt angle (bottom) of the molecules in self-assembled monolayers of F8H2 (circles) and H18 (squares) molecules as a function of the deposition time from liquid carbon dioxide mixtures. The lines are meant to guide the eye. The inset shows schematically the geometry of the near-edge x-ray absorption fine structure (NEXAFS) experiment.

