

Molecular orientation and grafting density in semifluorinated self-assembled monolayers of mono-, di- and trichloro silanes on silica substrates

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Introduction: Formation of self-assembled monolayers (SAMs) on material substrates has now become a routine way to tailor the surface properties of materials [1]. One of the outstanding issues concerning the application of SAMs is the organization of the molecules in the SAM. It has long been appreciated that the organization of the SAM molecules does not only influence the wetting properties of the SAMs but it is vital for their stability and weatherability. The packing of SAMs results from a complex interplay between the molecular nature of the SAM molecules and the type of bonding to the substrate; they both influence the tilt angle on the substrate and ultimately the grafting density of the SAM molecules. The goal of this work was to demonstrate that depending on the bonding environment around the silica atoms, the alkyl molecules adopt different orientations and grafting densities on flat silica-covered substrates [2].

Methods and Materials: We formed SAMs from 1H,1H,2H,2H-Perfluorodecyldimethylchlorosilane (m-F8H2), 1H,1H,2H,2H-Perfluorodecylmethylchlorosilane (d-F8H2), 1H,1H,2H,2H-Perfluorodecyltrichlorosilane (t-F8H2). A small amount of silane was placed on the bottom of a Petri dish, the silicon wafer was positioned above the silane source (distance ≈ 1 cm), the whole system was closed and kept at ambient conditions. After a predetermined period of time the wafer was taken out of the container, washed thoroughly with ethanol to remove physisorbed silane molecules and dried with nitrogen. Contact angle experiments were performed using a Ramé-Hart contact angle goniometer (model 100-00) equipped with a CCD camera, and analyzed with the Ramé-Hart software. The SAM thickness was measured using a variable angle spectroscopic ellipsometry (VASE) (J. A. Woollam, Co., Inc.). Experiments using the near-edge x-ray absorption fine structure (NEXAFS) spectroscopy were carried out on the NIST/Dow Soft X-ray Materials Characterization Facility at the NSLS BNL.

Results: We found that the kinetics of SF SAM formation during vapor deposition is faster than that of normal organosilane hydrocarbons [3]. We speculate that this faster kinetics is a consequence of stronger intermolecular interaction between the F8H2 moieties, relative to simple hydrocarbons. Results of NEXAFS spectroscopy experiments reveal that the molecular organization in F8H2-SAMs depends critically on the bonding environment around the silicon group. Specifically, while trichlorosilane-based molecules are oriented almost perpendicular to the silica substrate, the average tilt angle of F8H2 increases with increasing the number of the methyl groups attached to silicon (cf. Table I). This observation can be rationalized by considering steric hindrance present in the latter cases (cf. Figure 1). The molecular orientation elucidated from the NEXAFS spectroscopy measurements can be used to estimate the grafting densities of the F8H2 molecules on the substrates. Analysis using a simple one-dimensional geometric model reveals that the grafting density of m-F8H2 is approximately one half of that corresponding to the t-F8H2 SAM. We have also demonstrated the self-consistency of these results. Specifically, we have shown that the grafting densities of F8H2 determined from the one-dimensional chain tilt model are in accord with those that can be inferred from the relative edge-jumps in the fluorine K-edge NEXAFS spectra.

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References:

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Table I Molecular properties of SF SAMs

SAM	Thickness ^{a)} (nm)	$\langle\tau_F\rangle$ ^{b)} (deg)	σ_{F8H2} ^{c)} (nm ⁻²)	$\Delta I_{PEY,F}$ ^{d)} (a.u.)	$\sigma_{F8H2}/\Delta I_{PEY,F}$ ^{e)}
m-F8H2	0.9	45 +/- 3	1.59	0.045	35.3
d-F8H2	1.4	35 +/- 3	2.14	0.064	33.4
t-F8H2	1.65	10 +/- 2	3.09	0.105	29.4

^{a)} Thickness measured by VASE (assuming $n_{F8H2}=1.38$).

^{b)} Average tilt of the $F(CF_2)_8-$ measured by NEXAFS spectroscopy.

^{c)} Grafting density of F8H2 calculated from $\langle\tau_F\rangle$.

^{d)} Fluorine K-edge jump.

^{e)} Calculated from σ_{F8H2} and $\Delta I_{PEY,F}$ given in the table.

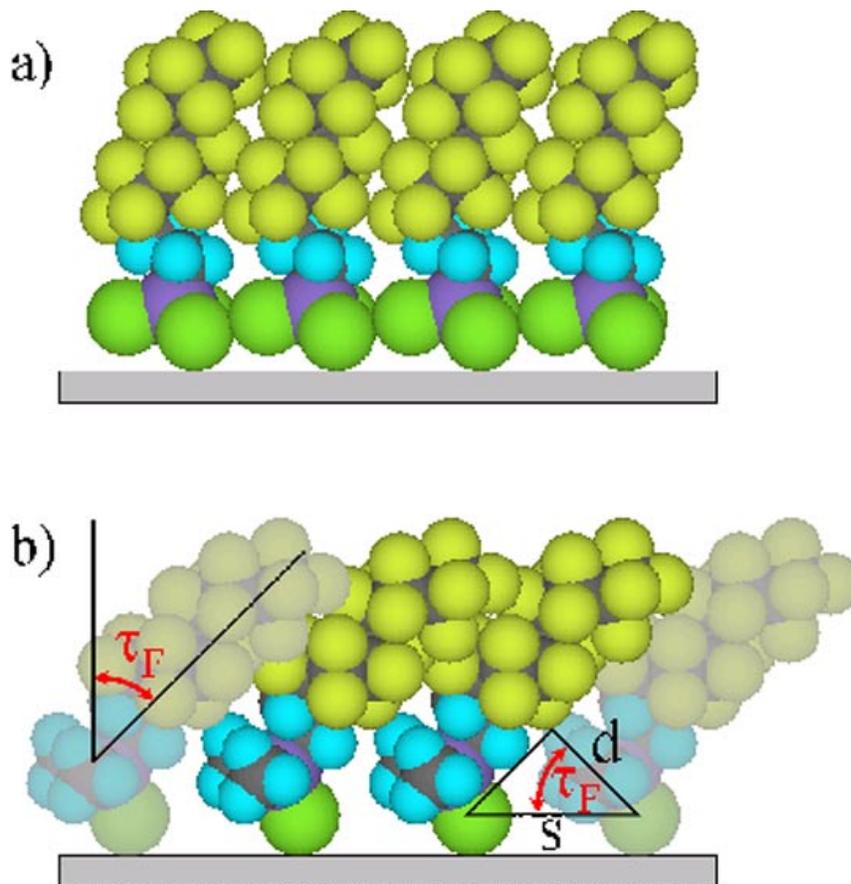


Figure 1 Schematic illustrating the molecular organization of t-F8H2 (a) and m-F8H2 (m) on silica substrates. Also shown is the geometry used to evaluate the distance between two neighboring F8H2 molecules, s , from the SF mesogen average tilt angle, $\langle\tau_F\rangle$, and the mesogen diameter, d .