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Thermal Behavior of Perfluoroalkylsiloxane Monolayers on the Oxidized Si(100) Surface

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The thermal stability of perfluoroalkylsiloxane monolayers in a vacuum is investigated via X-ray photoelectron spectroscopy (XPS) for temperatures up to 600 °C. 1H,1H,2H,2H,-perfluorodecyltrichlorosilane (FDTS) monolayers are deposited on oxidized Si(100) surfaces from the vapor phase with various degrees of surface coverage. Significant monolayer desorption is observed to occur at temperatures below 300 °C regardless of the initial monolayer coverage. The desorption mechanism follows first-order kinetics and is independent of the initial coverage. Removal of FDTS is found to occur by the loss of the entire molecular chain, as evidenced by the fact that the CF₃/CF₂ peak area ratios remain unaffected by the annealing process although CF_n/Si peak ratio declines with annealing. This is in sharp contrast to the behavior observed for octadecyltrichlorosilane monolayer for which elevated temperature leads to C–C bond breakage and successive shortening of the alkyl chain. It is also shown that the binding energy and the shape of the F 1s line are good indicators of the degree of disorder in the chain, as well as a measure of the interaction of the chain with the silicon surface.

Introduction

Self-assembly of thin organic coatings on solid surfaces is a well-studied process both due to its fundamental scientific interest and for its far-reaching technological applications.^{1,2} The formation of a self-assembled monolayer (SAM) film involves adsorption of a surface-active precursor molecule (from liquid or vapor phase). This step is typically followed by substantial cooperative reorganization necessary to maximize the interaction between the substrate and the surface-active moiety of the precursor molecules and to optimize the steric constraints and van der Waals interactions between the inactive moieties. While surface adsorption and SAM formation processes have been the subject of extensive investigation³, comparatively less is known about monolayer chemistry in harsh environmental conditions, such as under thermal stress, high impact, friction, wear, and radiation. Monolayer stability has great technological importance because the reliability of a device often depends critically on the integrity of its surface functionality imparted by a SAM coating.⁴ For example, in many microelectromechanical systems (MEMS), SAM coatings are employed to prevent failure by surface adhesion. The Texas Instruments DMD, a MEMS-based display chip lubricated by a perfluoroalkanoic acid, is an example of successful commercial use of SAMs.⁵ For the ubiquitous silicon-based MEMS devices, alkylsiloxanes are often chosen as lubricants.^{6,7} For such devices operating in a harsh environment, thermal stability of the SAM is of critical importance.

This paper describes investigations of the thermal behavior of perfluorinated alkylsiloxane monolayers, derived from the

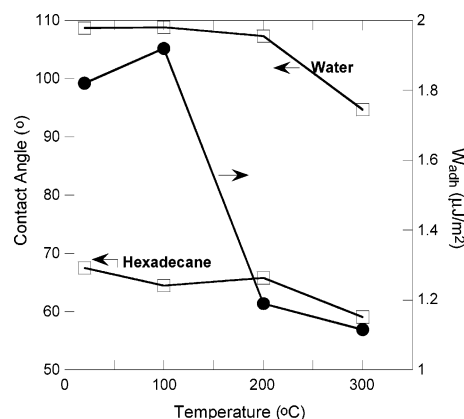


Figure 1. Temperature dependence of the water and hexadecane contact angles and corresponding work of adhesion for a microcantilever beam array coated with a FDTD monolayer.

precursor molecule 1H,1H,2H,2H,-perfluorodecyltrichlorosilane (FDTS), and self-assembled on the oxidized Si(100) surface from the vapor phase. These studies were prompted in part by the unexpected results of recent investigations of adhesion using microcantilever beam arrays (summarized in Figure 1).⁸ These MEMS devices, coated by FDTS SAMs and subjected to thermal cycling at temperatures up to 300 °C in air, showed an unexpected decrease in the apparent work of adhesion with increasing annealing temperature. This result is all the more surprising given that flat Si(100) control samples processed alongside and thus subjected to the same treatment as the microdevices, show a slight increase in the surface energy of the coatings, as deduced by water and hexadecane contact angle measurements. Annealing in a vacuum or inert ambient has very similar effect as annealing in air. The results shown in Figure 1, the technological relevance of the thermal stability of fluorinated alkylsiloxane SAMs, and the poor current understanding of some basic issues related to the different chemistries of hydrogenated and the perfluorinated alkylsiloxane SAMs^{9–11} all warrant a fundamental investigation of the thermal behavior of perfluoroalkylsiloxane monolayers.

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We have chosen X-ray photoelectron spectroscopy (XPS) in ultrahigh vacuum (UHV) as the primary technique for our investigations. Although XPS is known to degrade organic monolayers at high X-ray fluence¹² (because of the damage induced by photoelectrons and secondary electrons), this spectroscopy technique has the advantage of providing clear, distinct signatures for carbon in different bonding environments. For instance, the C 1s chemical shifts between CF₃, CF₂, and CH₂ groups are 2 eV or larger, owing to the partially ionic nature of the C–F bond, and smaller but equally significant chemical shifts are observed for carbon 1s in the bonding configuration CH₂–CF₂ vs CH₂–CH₂ or C–Si. In contrast, hydrogenated monolayers are best studied by vibrational spectroscopies (such as FTIR or HREELS). Unfortunately, vibrational techniques are not as useful in the study of perfluorinated monolayers. This is because the similar mass of C and F atoms tends to make the normal modes of vibration of the molecules delocalized through the whole perfluorinated chain. Thus, the assignment of vibrational modes to localized bond vibrations in fluorocarbon molecules is neither easy nor very meaningful (it is impossible to assign distinct frequencies, for example, to the C–F bond stretch in CF₃ as opposed to the stretches in CF₂¹³). This problem mirrors somewhat the unsuitability of XPS to study the chemistry of fully hydrogenated SAMs due to the lack of significant chemical shifts of the carbon 1s line in different C–H_n bonding configurations.

The main results of this work are summarized hereafter: (a) noticeable loss of fluorine takes place upon even moderate annealing (100–200 °C), regardless of initial film coverage; (b) this loss is attributed to desorption of entire loosely bound perfluorinated chains (such as physisorb chains); (c) this loss is accompanied by a shift in the position of the F 1s line, likely caused by tilting of the remaining well-anchored chains (the present work provides, to our knowledge, the first direct recognition of this shift); and (d) the integrity of the perfluorinated chains remaining on the surface is maintained in UHV at least up to temperatures in excess of 600 °C.

Experimental Section

Materials, Coating Procedure, and Annealing Sequence. The monolayer precursor 1H,1H,2H,2H-perfluorodecyltrichlorosilane, (CF₃(CF₂)₇(CH₂)₂SiCl₃) was obtained from Lancaster Synthesis (96% purity) and used without further purification. Deionized (DI) water (Nanopure system) with a resistivity of 18 MΩ was used. Reagents used in vapor coatings underwent several freeze–pump–thaw cycles before use. Monolayer deposition in the vapor phase was done as follows. Si(100) substrates were degreased in acetone and treated in UV-ozone for 20 min, and the native oxide was removed by etching in HF. The substrates were put in a low-pressure reactor⁸ where oxygen plasma was applied (3–4 min, 300 mTorr, 50 W) followed by water plasma (3–4 min, 300 mTorr, 50 W). A FDTS vial was then heated using boiling water, and the vapor was introduced in the reactor (to reach 450 mTorr). Water vapor was then dosed to reach a total pressure of 1.2 Torr. After 20 min, the system was pumped down and this operation was repeated until a good quality coating was obtained on the surface as evidenced by contact angle measurements. FDTS samples with lower coverage were produced by reducing the total number of dosing cycles. After the last deposition cycle, the samples were left under vacuum overnight.

Table 1. Initial Coverage of the Different Samples Used, as Well as Their Corresponding Annealing Temperatures^a

sample	F(1s)/Si(2p) _o	% coverage	tested at temps (°C)
1	0.72	80%	RT, 100, 300, 450
2	1.30	135%	RT, 300, 450, 550
3	0.93	97%	RT, 100, 400, 500, 600
4	0.60	63%	RT, 100, 250, 350, 450, 550
5	0.70	72%	RT, 400, 500, 600
6	0.74	77%	RT, 600

^a The coverage of sample 2 is over 100%, probably due to the presence of a partial bilayer or agglomerates.

Static contact angle was measured after each deposition cycle on a dedicated Si(100) test chip to monitor the progression in the monolayer coverage. Static contact angle measurements were performed with a Ramé–Hart 100A goniometer using DI water (18 MΩ) and spectroscopic grade hexadecane.

The chips to be used for the annealing experiments were transferred quickly from the deposition chamber (exposure to ambient air lasting no longer than 5 min) to the XPS load lock chamber and were kept under UHV thereafter. Afterward, room temperature (RT) spectra were obtained to establish the initial surface coverage. Different annealing sequences were performed on different samples, both to explore the effect of different initial coverage and to avoid subjecting a single chip to excessive X-ray exposure. Each annealing step consisted of raising the temperature to a target value (ramp time ≈ 10 min) where they were kept for 5 min before being cooled back to RT for XPS analysis. At most, five annealing steps were performed on a single sample. Table 1 summarizes the annealing sequences performed on the various samples reported here.

Photoelectron Spectroscopy. XPS was used to characterize the chemical composition and bonding configuration of the monolayer coatings. Photoelectron spectra were acquired in a UHV chamber (base pressure 10^{−9} Torr) using a hemispherical analyzer (Omicron EA125) and a non-monochromated dual excitation (Mg Kα or Al Kα) source (DAR400, operating at 15 kV voltage bias and 20 mA emission current) at a 70° angle from the detector. The source line width is approximately 1.4 eV fwhm, as calibrated with the Au 4f_{7/2} line. The takeoff angle was kept fixed along the surface normal in all experiments. Since all recorded spectra were obtained from monolayers deposited on single crystalline Si wafers, binding energies are conveniently referred to the elemental Si 2p line at 99.3 eV.

High-resolution (0.1 eV) spectra were obtained for the F 1s, O 1s, C 1s, and Si 2p regions. Background subtraction was effected following Shirley's method.¹⁴ Peak areas are used to compute elemental ratios¹⁵ after correcting for analyzer transmission,¹⁶ photoionization cross sections,¹⁷ and extinction of the photoelectrons as they travel through the monolayer.¹⁸

As stated previously, exposure of the SAM to X-rays can cause significant film degradation at high doses because of film damage and desorption induced by photoelectrons and secondary electrons. Under the X-ray fluence used in our experiments, the F loss (quantified through the F/Si ratio) of about 30% per hour of exposure was measured. Therefore, to minimize the damage, the duration of each scan was limited to about 5 min and the spectral acquisition to the four regions indicated above.

Quantum Chemical Calculations. Calculations of the electronic structure of the FDTS precursor molecule were performed using GAUSSIAN 98.¹⁹ Configurations were optimized using density-functional theory (DFT) with the three-parameter Becke–Lee–Yang–Parr²⁰ hybrid functional to calculate exchange and correlation energies. Different basis sets were chosen depending on the atoms:

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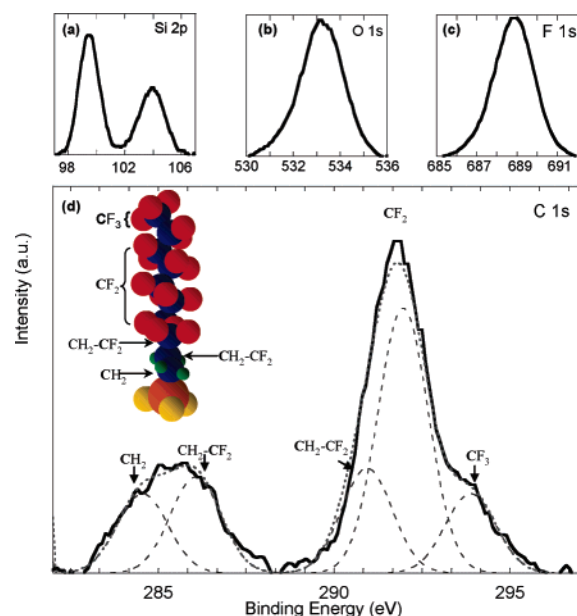


Figure 2. Initial XP spectra from sample 3 prior to any annealing. (a) Si 2p, (b) O 2s, (c) F 1s, and (d) C 1s with Gaussian fits to five peaks (CH_2 , $\text{CH}_2\text{-CF}_2$, $\text{CF}_2\text{-CH}_2$, CF_2 , CF_3). Inset: Schematic of the FDTD molecule indicating the various contributions for the C 1s line.

for F, C, and Si atoms, the 6-31G basis set were adopted, while H atoms were described with the STO-3G basis set. Chemical shifts were obtained from the calculated molecular orbital energies by invoking Koopman's theorem.²¹

Results and Discussion

1. XPS Measurements and Analysis. Survey XP spectra of FDTD monolayers show strong photoemission (PE) lines grouped in four ranges of binding energy (BE), in addition to various Auger peaks, and weaker PE lines such as Si 2s and O 1s. The four spectral regions of interest are, in order of descending BE, 685–692 eV, corresponding to F 1s photoelectrons, 530–536 eV (O 1s), 282–298 eV (C 1s), and 97–107 eV (Si 2p). To limit the exposure of each sample to the X-rays, the evolution of the XP signal was followed with annealing temperature by acquiring high-resolution spectra only in the four regions of interest.

1.1. Si 2p Region. Two peaks are observed in this region, corresponding to uncharged elemental Si (99.3 eV) and to Si^{4+} in SiO_2 (103–104 eV) (Figure 2a). No change is observed in the Si 2p region upon annealing for any given sample. Small sample-to-sample differences in the SiO_2 peak intensity and position (both measured relative to the Si peak at 99.3 eV) reflect small differences in the thickness of the oxide layer and in the SiO_x transition layer between Si and SiO_2 .

1.2. O 1s Region. Similarly to Si 2p, the O 1s (shown in Figure 2b) region also shows little change upon annealing, confirming that the oxide and possible traces of water left behind

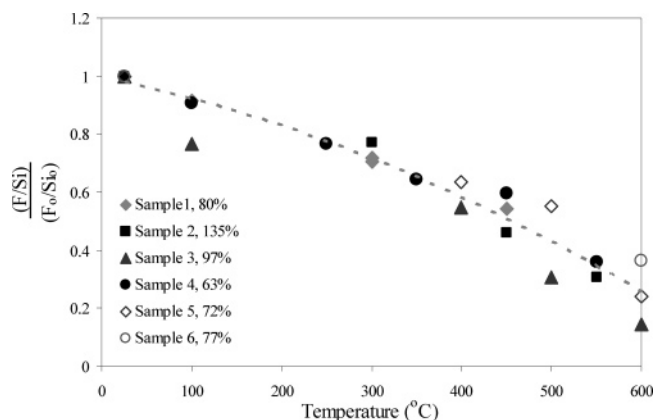


Figure 3. Temperature desorption of the FDTD monolayer as evidenced by the change in the ratio of the F 1s/Si 2p peak areas. Different symbols correspond to the different samples investigated.

from the monolayer condensation process play no active role in monolayer degradation and desorption.

1.3. C 1s Region. Figure 2d shows a typical close-up spectrum of the C 1s region for a well-packed FDTD monolayer before annealing (sample 3). The C 1s region displays three main spectral features, namely (1) a peak around 285.5 eV, (2) a peak around 291.5 eV, and (3) a peak at 293.5 eV (usually showing up as a pronounced shoulder on the 291.5 eV peak). The first peak is rather broad and is attributed to the presence of (at least) two unresolved PE lines: one from the first C atom (bonded to Si) and one from the second C atom (bonded to the first fluorinated carbon, hereafter denoted as $\text{CH}_2\text{-CF}_2$). Intensity in this region can in principle originate from two additional sources: adventitious carbon contamination (typically contributing an a priori unknown intensity in the region 284–285 eV) and, for Mg K α source, an X-ray satellite of the peak at 292 (showing up at –8.4 eV lower BE with intensity equal to 8.0% of the primary peak). The signal drops to zero in the region between 287 and 289 eV, after which it rises again to produce a broad peak centered around 291.5 eV. This second peak is assigned to CF_2 .⁹ Its width suggests that it, too, results from the superposition of two or more unresolved peaks. Ohnishi et al.¹⁸ assign a peak at about 290.5 eV to carbon in the CF_2 group bonded to CH_2 , that is, to $\text{CH}_2\text{-CF}_2$ following the established notation. The remaining intense peak centered at 291.8 eV is assigned to the other CF_2 groups of the FDTD chain. Last, the peak at 293.5 eV is assigned to carbon in CF_3 .¹⁵ Figure 2d also shows the C 1s region fitted with all five peaks mentioned (two peaks for the 283–286 eV region and three peaks for the 288–295 eV region). The inset of Figure 2d displays the corresponding position of the various XP peaks on the FDTD molecule.

From the analysis of the C 1s spectra of all samples, the CF_3/CF_2 ratio (i.e., the peak area at 293.5 eV to that at 291.5 eV) is found to remain essentially constant at 0.22 ± 0.03 after annealing up to 500 °C independent of the initial coverage, despite the observed decrease in the total F/Si ratio (Figure 3). This indicates that the loss of fluorinated species occurs by desorption of the entire fluorinated moiety, likely the entire precursor molecule. This scenario is in contrast with the behavior observed by vibrational spectroscopy for hydrogenated monolayers, such as octadecyltrichlorosilane (OTS),^{22,23} which are found to degrade by cleavage of the C–C bond, such that upon heating (to 475 °C), the monolayer begins to shorten successively from the top

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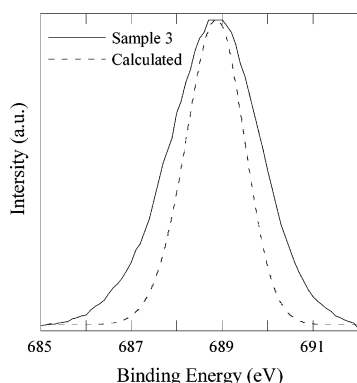


Figure 4. Measured and calculated F 1s XP spectra for sample 3. The intensity and peak position of the calculated spectra were modified to fit the measured XP spectra. A fwhm of 1.4 was added to the binding energies of all the F atoms on the FDTS to reflect the dispersion of the spectrometer.

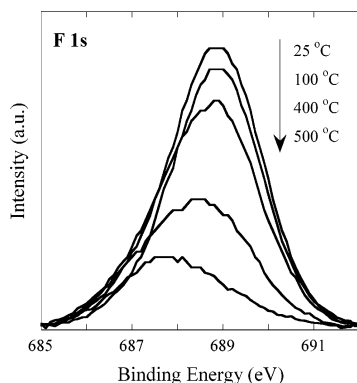


Figure 5. Observed variations caused by annealing in the shape and position of the F 1s line for sample 3. The initial fwhm is 2.37 eV and the peak position is 688.8 eV, while the final fwhm is 2.80 eV and the peak position shifts to 687.9 eV.

until the Si—C bond is reached. A similar CF_3/CF_2 ratio is obtained for annealed well-packed monolayers deposited from solution.⁸

1.4. F 1s Region. The F 1s region of a well-packed monolayer is shown in Figure 2c. The F 1s/Si 2p total peak area ratio is a direct measure of monolayer coverage. According to Ohnishi et al.,¹⁸ after factoring the photoelectron cross sections, this ratio has a value of about 1 for Langmuir–Blodgett monolayers transferred at pressures just below the collapse pressure (tightest packing). Similar coverages are obtained for well-packed monolayers deposited from the vapor phase or solution.⁸

We have measured the F 1s/Si 2p ratio as a function of annealing temperature for various samples with different initial coverages. Somewhat surprisingly, significant loss of fluorine is observed after annealing to even moderate temperatures, even for highly packed monolayers. After the measured values were normalized to each sample's initial coverage, the data for all samples can be seen to fall on the same curve, as shown in Figure 3. This scaling signifies that desorption follows first-order kinetics, that is, the desorption rate is linearly proportional to coverage, and thus, it is independent of chain–chain interactions and packing details.

In addition to coverage information, the F 1s line encompasses a signature of the chemical state of the perfluorinated chains, as shown by a broadening beyond the intrinsic X-ray source width, a nontrivial line shape, and shift in BE upon annealing (Figures 4 and 5). These features do not appear to be attributable to the change in BE of the F 1s orbitals with position of F atoms along the chain of the FDTS molecule. Broadening of the line width is illustrated by comparing the measured F 1s peak width with

the predicted peak obtained from the ab initio calculations (a 1.4 fwhm Gaussian was imposed on the calculated binding energies of all the fluorine molecular orbitals to represent the X-ray source broadening). The resulting calculated F 1s line shape has a fwhm of 1.54 eV, much smaller than the measured width of the fluorine peak which varies between 2.3 and 2.7 eV. This effect is shown in Figure 4, where the calculated F 1s line shape is plotted along with the experimental spectrum from sample 3. The additional broadening (0.8 eV) of the experimental line suggests an effect of the local environment.

The effect of the local environment on the F 1s line shape is further demonstrated by observing the evolution of the F 1s line shape as a function of annealing temperature (Figure 5). For all samples studied, annealing has two main effects on the F 1s line (in addition to the predictable decrease in intensity due to chain desorption): the F 1s shifts to lower BE and broadens upon annealing. These effects are shown for sample 3 in Figure 5; for comparison, the initial fwhm is 2.37 eV and the peak position is 688.8 eV while the final fwhm is 2.80 eV and the peak position shifts to 687.9 eV. Chen et al.²⁴ observed a similar effect upon annealing of perfluoroalkanoic acid monolayers on alumina surfaces and attributed the effect to formation of oxyfluoride species, AlF_xO_y . This is unlikely to be an explanation for our experimental results. First, there is no evidence that a chemical reaction has taken place between F and Si and/or O, as no shifts are observed upon annealing in the PE lines of those elements. Furthermore, the lowering of the F 1s BE (peak position shifts to lower BE) indicates that F is reduced, not oxidized, as should be the case if, say, oxygen is inserted in the C—F bond to form C—O—F. Last, using the CF/Si ratio, instead of the F/Si, yields the same results as shown in Figure 3, indicating that the desorption of the chain is followed by an equivalent loss of fluorine, further supporting that F is not directly bonding to the substrate.

A possible explanation of the various F 1s line shape effects can be found if the interaction of the FDTS chains with the negatively charged silica surface is considered. Upon annealing and desorption of some of the FDTS chains, the remaining chains tilt away from the nearly vertical arrangement of a well-packed monolayer.⁶ Thus, the molecular orbital energy of some of the F atoms is raised by the proximity with the electron-rich silica surface, resulting in a smaller observed BE. Therefore, the effect of substrate interaction would imply a shift in BE for an originally loosely packed film (one where the chains are not all vertically oriented), *regardless of the annealing history*. Indeed, we have observed this phenomenon before annealing in a sample that was deliberately exposed to a reduced dose of FDTS to achieve submonolayer coverage of 60% (sample 4 in Table 1). Figure 6 shows the evolution of the F 1s signal for this sample as a function of annealing temperature. The initial asymmetry can be readily observed and can be fitted by two peaks, centered at about 687.5 and 689.1 eV, which can be attributed, respectively, to chains that are lying flat on the surface and chains that are *all trans*. As the annealing sequence proceeds, most of the intensity is lost in the higher-BE peak. Therefore, careful analysis of the F 1s peak reveals important characteristics of the monolayer and its interaction with the substrate, as well as how the interaction with the substrate evolves during the annealing process.

2. Relation between Monolayer Structure, Thermal Stability, and Adhesion Measurements. The thermal stability of FDTS monolayer coatings is dictated by the nature of the precursor molecule and by the way it affects the structure of the assembled

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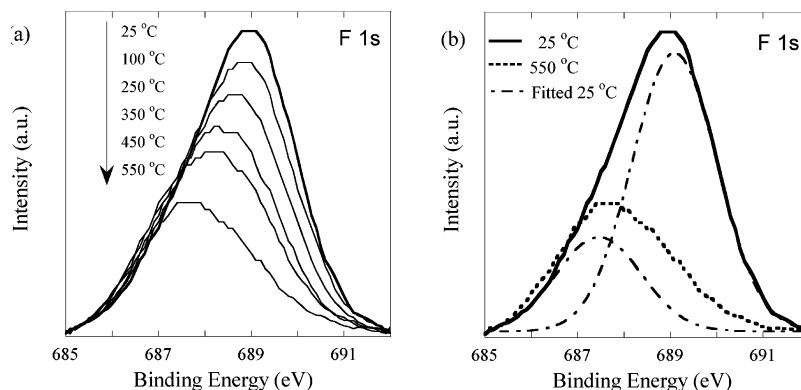


Figure 6. Observed variations caused by annealing in the shape and position of the F 1s line for sample 3. (a) Effect of annealing. (b) Measured F 1s line for RT and 550 °C, as well as two-peak fit for the room-temperature data (dashed lines).

film. Alkylsiloxanes are known for their propensity to form strong covalent bonds to hydroxylated surfaces and to one another by a condensation reaction. While these reactions happen simultaneously and competitively in hydrogenated alkylsiloxanes, we suggest that cross-linking is largely prevented in perfluoroalkylsiloxane SAMs because of the larger size of the F atom compared to the H atom (the length of the Si—O—Si bond is 0.32 nm,²⁵ while the distance between Si atoms for a FDTS molecule is 0.56 nm¹⁰). Therefore, only a fraction of the FDTS molecules are able to make strong covalent bonds to the surface, while the remaining molecules that complete the full monolayer arrangement are bonded by the much weaker van der Waals interaction or hydrogen bonding or possibly by very highly strained covalent bonds. It is likely that these weakly bound molecules give rise to significant desorption at temperatures between 100 and 300 °C. This is a similar argument as the one proposed by Sniegowski and de Boer²⁶ for the poor adhesion performance of FDTS at high humidity.

These results are in a sharp contrast to the findings of Kluth et al. for hydrogenated alkylsiloxane SAMs (such as OTS),^{22,23} which are found to desorb by a mechanism of radical chain decomposition at much higher temperatures (475 °C) and where, according to the authors, the thermal stability of these monolayers is not determined by the headgroup bonding configuration (e.g., cross-linking Si—O bonds) but rather by the Si—C or C—C bonds. As described above, this difference can be attributed to much more complete bonding to the substrate and cross-linking in these hydrogenated monolayers.

The results of adhesion and surface energy measurements reported in previous work and summarized in Figure 1 can be rationalized easily in view of the findings of our XPS experiments. On one hand, the reduction in water and hexadecane contact angle upon annealing can be explained by the disorder caused by desorption of weakly bound chains. On the other hand, the decrease in adhesion can be viewed in light of the removal of unreacted siloxane headgroups during the annealing process (nanometer-sized contacts commonly obtained during actuation in Si—based MEMS can pierce through the monolayer and their interaction with unreacted siloxane groups would contribute significantly to the measured adhesion). Tilting of the monolayer during the annealing process would therefore decrease the apparent work of adhesion and decrease the water and hexadecane contact angles.

Finally, the implications of the poor cross-linking of FDTS monolayers are not limited to stiction. It also has adverse effects for the film's ability to maintain its hydrophobicity when

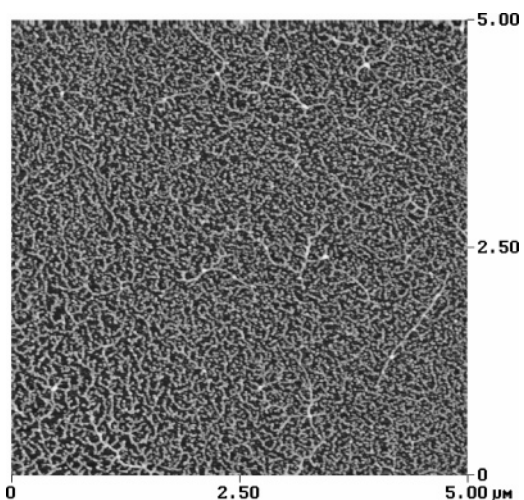


Figure 7. Tapping mode AFM image of a FDTS film after immersion in water for 6 weeks. A weblike structure indicative of the reconfiguration of the monolayer is clearly visible. The *z* scale is 10 nm.

immersed in water.²⁷ Figure 7 shows an AFM picture of a FDTS monolayer on Si(100) after immersion in water for 6 weeks. A weblike structure is clearly visible and is assumed to arise from desorption and cross-linking of FDTS chains away from the surface.

Conclusions

The thermal stability of perfluorinated alkylsiloxane monolayers was investigated using X-ray spectroscopy. Removal of the whole fluorocarbon chain was identified as a possible desorption mechanism due to a CF₃/CF₂ ratio that is kept constant during the annealing process. Desorption was observed for annealing at temperatures as low as 100 °C. First-order kinetics, independent of monolayer packing, was proposed from measurements of desorption of monolayers with different initial coverages. Finally, it was shown that the position, shape, and symmetry of the F 1s line was a good indicator of disorder in the monolayer.

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