

Orientation and Self-Assembly of Hydrophobic Fluoroalkylsilanes

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Fluoroalkylsilanes (FAS) prove to be an interesting water-repellent coating for the recently discussed "superhydrophobic surfaces". The FAS investigated here form a self-assembled monolayer when brought into contact with a surface. They arrange at a high degree of orientation with their molecular axis perpendicular to the substrate surface. The film stability and the film thickness were observed using X-ray photoelectron spectroscopy. The orientation of the FAS molecules was investigated with polarization-dependent X-ray absorption near edge spectroscopy (XANES). Furthermore using density functional theory the molecular structure was calculated in order to aid in the interpretation of the polarization dependence of the XANES spectrum at F K-edge.

1. Introduction

Hydrophobic behavior of a surface can be due to a chemical coating or due to a special microstructure minimizing contact area between the water drops and the surface. Obviously if both effects are combined and a structured surface, containing holes and pins vertical to the surface, is coated with a hydrophobic chemical in addition, drops of water can show contact angles of more than 150°. ^{1–3} These surfaces are called "superhydrophobic". With such extreme contact angles the drops of water are shaped nearly spherical and show a different behavior of floating. The drop of water is able to "roll" on the surface. While "rolling", it can bond and drag dirt. Surfaces such as this are called "self-cleaning surfaces". ⁴ The production of such hydrophobic structured surfaces is of high commercial interest. The need of chemical coatings combining the ability to bind strongly to the surface and an additional hydrophobic behavior is evident. To preserve the underlying microstructure of the surface, it is important to control the properties such as film thickness, orientation, and stability of the molecules. In this paper we present the analysis of the thickness and the orientation of a self-assembled coating of hydrophobic fluoroalkylsilanes (FAS) on various substrates obtained by X-ray photoelectron spectroscopy (XPS) and X-ray absorption near edge spectroscopy (XANES) measurements. Additionally we compare our experimental results with a calculated XANES spectrum based on density functional theory.

We think that our results concerning the chemical bond of FAS to the surface can be transferred to other silanes which form a silicon hydroxide group for the surface reaction as well. Even molecules with reactive groups instead of the passivated fluoroalkyl group, e.g., with a functional group that acts as a primer for other substances, may show a similar anchoring behavior at the surface.

2. Structure and Properties of the Self-Assembled Hydrophobic Coatings

The surfaces are coated by exposing them to an aqueous solution of FAS. Therefore we used the fluid tridecafluorooctyltriethoxysilane, C₈F₁₃H₄Si(OCH₂CH₃)₃, which contains silicon ethoxide as a functional group. By hydrolysis it reacts with water to form silicon hydroxide as a reactive group at the end of the molecule, which is responsible for the chemical bond with the substrate as reported by the provider Degussa Hüls AG. ⁵ The fluoroalkyl group is the hydrophobic part of the molecule. The exact geometry and the electronic structure of the molecule were not found in the literature. Therefore (and for the interpretation of the polarization dependent XANES simulation, as stated below) we have calculated the chemical bonds using the density functional theory. ^{7,8} Starting with a singlet electronic configuration C₈F₁₃H₄Si(OH)₃ molecule, the geometries were fully optimized within the local density approximation, using a polarized valence triple- ζ basis set (H), ⁹ polarized split-valence 6-31G basis sets (O, F, C), ¹⁰ and an effective core potential including double- ζ valence functions (Si). ¹¹ All the calculations were carried out using the Gaussian 98 ¹² program on a Cray J90 parallel

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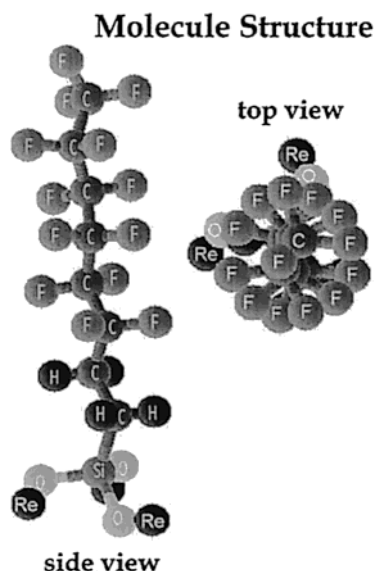


Figure 1. Structure of $C_8F_{13}H_4Si(ORe)_3$ molecule. The C–F bonds act as the hydrophobic part of the molecule. The Si(ORe)₃ acts as anchor at the substrate.

vector processor system. Figure 1 shows a picture of the calculated molecular ground-state geometry which is found to be helical.

From this molecular structure one would expect that the molecule is bound to the substrate via the reactive silane end with virtually no interaction between the neighboring fluoroalkyl tails. This model furthermore suggests a maximum stable thickness of one monolayer.

Regarding the hydrophobic behavior, we are not able to present contact angle measurement at this time. But we can estimate from visual observation that a drop of water on a plane Si surface covered with FAS shows a static contact angle of approximately 90°. For a microstructured Al_2O_3 membrane⁶ a drop of water appears to be nearly spherical. We estimate a static contact angle in excess of 145°.

3. Experimental Section

3.1. XPS. To determine the film thickness, XPS measurements of FAS coatings on indium tin oxide (ITO) substrates were prepared. The photoelectron spectra were measured using

monochromatized Al K α X-rays and a hemispherical electron analyzer EA200 with integrated electron detector MCD200 manufactured by Leybold AG. All measured kinetic energies were converted to a binding energy scale with the Fermi level as a reference. The electron spectroscopy is a surface-sensitive method. The information depth depends on the kinetic energy of the electrons due to their escape length from the material. Therefore the peak intensities of the XPS spectra may be used to get information of the film thickness of the FAS. The intensities of the F1s electrons in XPS of different samples were measured in normal emission and normalized to the In3p_{3/2} peak of the ITO substrate. By comparison to the F1s intensities of a CaF₂ film of known thickness, we obtain the absolute amount of fluorine atoms and hence the number of molecules per surface area. The FAS molecules were brought onto the ITO substrate by dip coating. To obtain a rough estimate of the stability, after coating the samples were rinsed subsequently using various methods: 5 min ultrasonically in water, 15 min ultrasonically in propanol, 15 min ultrasonically in acetone, and at least 10 times mechanically rubbing with H₂O-wet cleaning pads.

3.2. XANES. Polarization-dependent XANES measurements were used to determine the orientation of the molecules with respect to the surface. The measurements were done at the BESSY I synchrotron facility in Berlin using the PM5 beamline. In XANES a core level electron was excited to the unoccupied states. Therefore the absorption cross section depends on the density of the unoccupied states and can be measured via the electron yield as a function of the photon energy. The total electron yield of the sample was measured using a Channeltron, and the incoming photon flux was measured using the current of a gold grid. The absorption of the linear polarized photons depends on the orientation of the molecular bonds. By varying polarization vector relative to the substrate surface, one is able to detect a dominant orientation of molecular bonds relative to the substrate surface. In our experiment this was done by changing the polarization angle θ ($10^\circ \leq \theta \leq 90^\circ$) between the polarization vector and the surface normal. For XANES, ultrasonically cleaned plane Si wafers and microstructured Al_2O_3 membranes (200 nm channels)⁶ were used as substrates. The samples were prepared by dip coating. For the XANES measurements all samples were 15 min ultrasonically cleaned in ethanol after coating.

4. Results

4.1. Thickness. Figure 2 shows the photoelectron intensity of the fluorine 1s signal as a function of the binding energy. The F1s peak intensity decreases after the first three cleaning steps. The decrease represents the delamination of weakly bound FAS molecules. After these initial cleaning steps, the curves show the same F1s

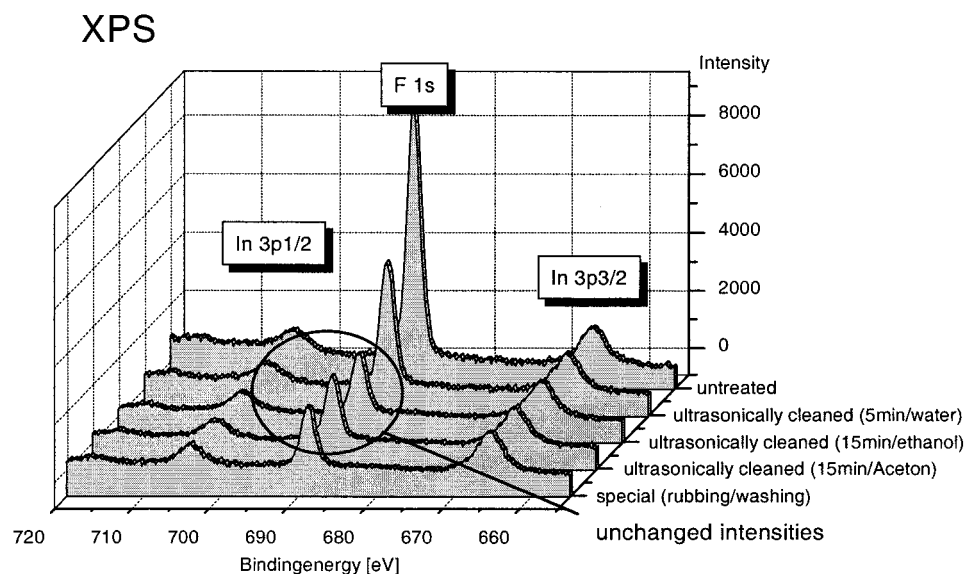


Figure 2. XPS spectrum of FAS on plane ITO substrate. Spectra are normalized to the In3p_{3/2} peaks. After initial cleaning steps, the number of molecules on the surface is not reduced by subsequent cleaning steps.

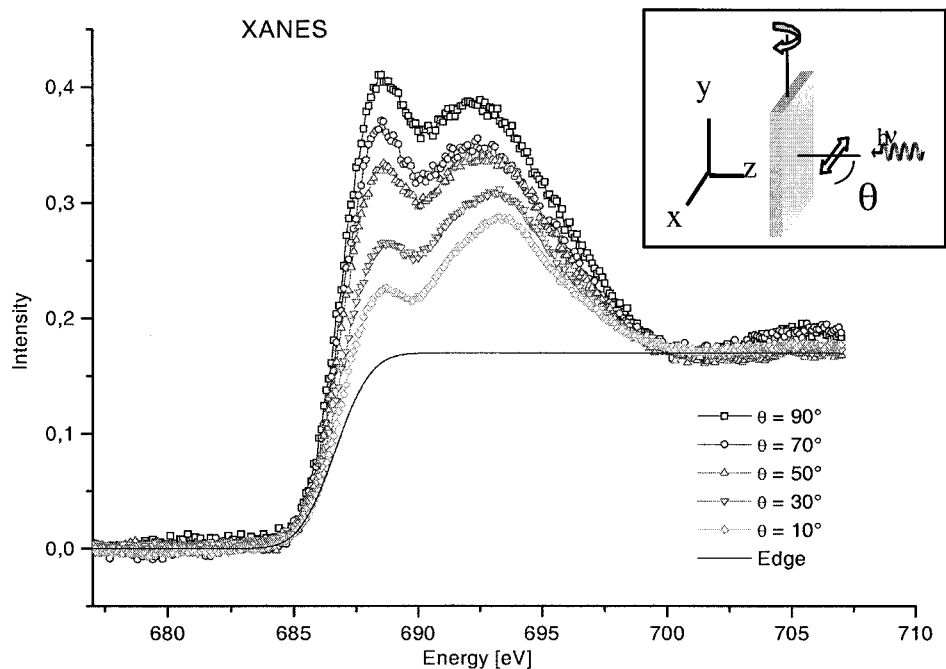


Figure 3. F K-edge spectra of a FAS sample on a Si substrate. Spectra were taken with different polarization angles θ (inset).

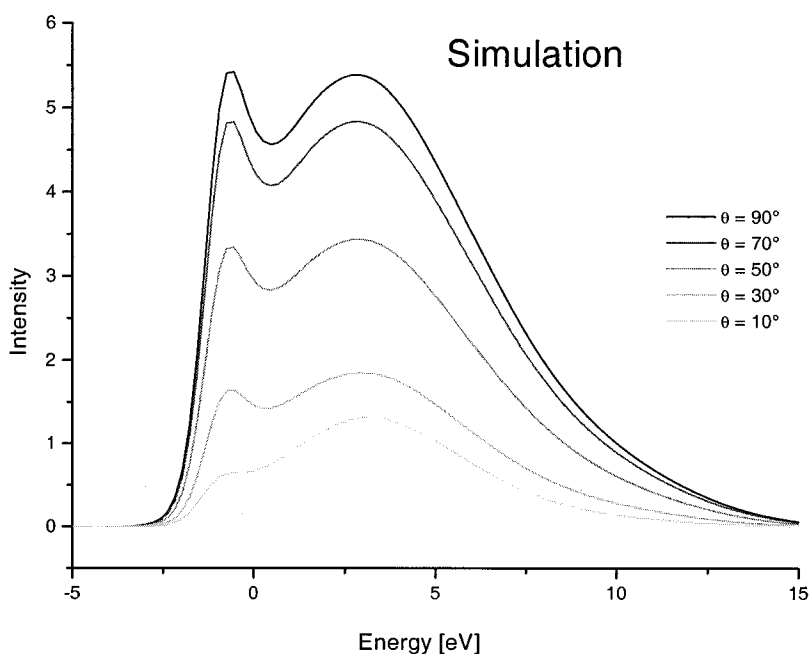


Figure 4. Calculated fluorine K-edge spectra at different polarization angles. Assumed is a single FAS molecule with perpendicular orientation on a planar surface.

intensities. This corresponds to a strongly bound layer of FAS molecules on the substrate. Even mechanical rubbing or washing by acetone or propanol does not remove this layer. The coverage of this layer can be estimated by comparison of the XPS intensity of a thin CaF_2 film with a known thickness.¹³ The quantitative analysis shows that the number of fluorine atoms detected is comparable with the calculated number of fluorine atoms in a monolayer of FAS molecules. From this we deduce a 75% coverage if a closed packed hexagonal structure is assumed for the monolayer.

4.2. Orientation of the Individual Molecules. Figure 3 shows the K absorption spectrum of fluorine of a self-

assembled monolayer of FAS at different polarization vectors relative to the substrate. Due to dipole selection rules the strength of the observed transition depends on the angle between the polarization vector of the X-ray radiation and the bond axis of each C–F bond. Consequently the variation of the relative peak intensities for different orientations of the polarization vector of the light can be used to determine the orientation of the molecular axis. The XANES spectra taken by varying the angle θ between polarization vector and surface normal are shown in Figure 3. For example $\theta = 90^\circ$ means that the surface normal of the substrate is parallel to the z -axis (inset Figure 3). A strong polarization dependence is evident and demonstrates the high amount of oriented molecules in the layer. An exact analysis of the data shows that the

(13) CaF_2 standard was deposited on a cleaned Si wafer; the thickness was controlled by an quartz-crystal oscillator.

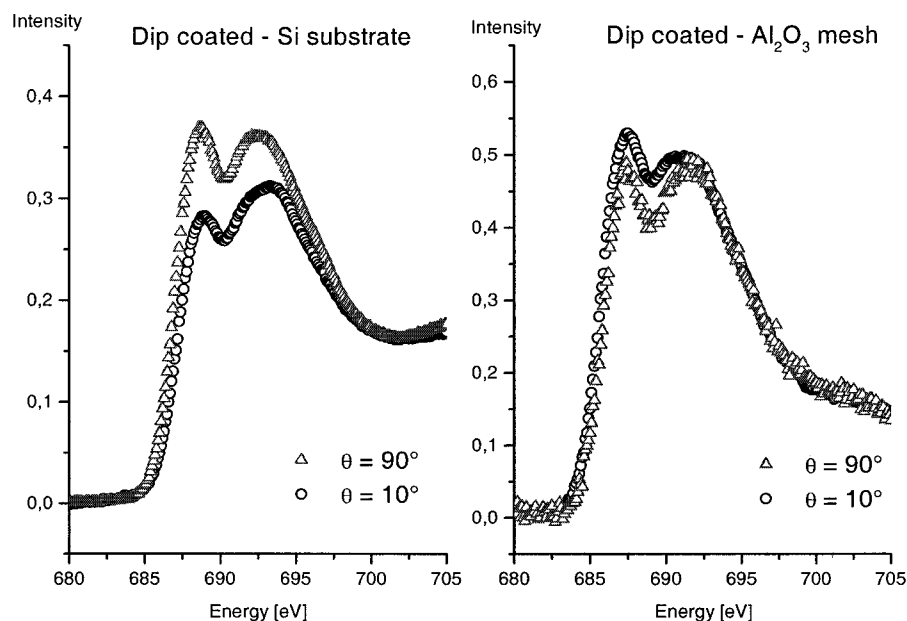


Figure 5. Left: F K-edge spectra of a FAS sample on a planar Si substrate. Right: F K-edge spectra of a FAS sample on a Al_2O_3 membrane (200 nm channels).

molecular axis (MA) is predominantly oriented perpendicular to the substrate surface. To confirm the perpendicular orientation on the surface, a calculation of a FAS molecule with perpendicular orientated MA on a planar surface was done. The absorption signal for the different polarization angles was calculated assuming p-like excited states. The results of the simulation are given in Figure 4. Both calculated and measured spectra show the same angular dependence, indicating that our geometric model of the molecular orientation on the substrate is correct. Note that for comparison of Figure 3 and Figure 4 it has to be considered that in the calculation no excitations into continuum states ("atomic-like absorption", see solid line in Figure 3) are included. Nevertheless, the expected and measured dependence of XANES spectra at the F K-edge for different polarization angles is well reproduced by the calculation.

The high degree of molecule orientation observed in XANES indicates that a polymerization over several layers is unlikely. The sensitivity of this measurements is apparent from the change of the angular dependence. Due to the different chemisorption properties of the first and all subsequent layers, it is highly unlikely that island formation occurs. Furthermore the second and all additional layers would not be ordered.

4.3. Structured Surfaces. The absorption spectra of FAS on a structured Al_2O_3 surface are shown in Figure 5. These spectra exhibit an inverse polarization dependence compared to the planar surface. This indicates that the molecules are partly oriented parallel to the macroscopic surface. This can be understood if one considers that they are bound perpendicular to the channel surface.

Even inside the channels the molecules are oriented perpendicular to the channel surface resulting in their MAs being oriented perpendicular to the z -axis (inset of Figure 3). For the absorption signal the maximum excitation probability should be measured for $\theta = 10^\circ$. In our experimental setup the smallest possible angle was $\theta = 0^\circ$. The less pronounced angular dependence between $\theta = 10^\circ$ and $\theta = 90^\circ$ is attributed to FAS molecules located outside the channels on the surface with their MA parallel to the z -axis.

5. Conclusion

We observed a strong bond between the first monolayer of dip-coated FAS molecules and the substrate. In this self-assembled monolayer we found the MA predominantly oriented perpendicular to the substrate surface. Even in the microchannels of an Al_2O_3 membrane this orientation is observed. The model calculation using the density functional theory is in excellent agreement with our measured XANES data. Dependent on the dip-coating process further layers can be weakly bound to the first layer. These upper layers can be removed easily by rinsing the sample in water or ethanol.

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