

Induced Orientational Order in Long Alkyl Chain Aminosilane Molecules by Preadsorbed Octadecyltrichlorosilane on Hydroxylated Si(100)[†]

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We studied the adsorption of (17-aminoheptadecyl)trimethoxysilane (AHTMS; $\text{NH}_2(\text{CH}_2)_{17}\text{Si}(\text{OCH}_3)_3$) onto hydroxylated Si(100) wafers, which were preexposed to methyl-terminated *n*-octadecyltrichlorosilane (OTS; $\text{CH}_3(\text{CH}_2)_{17}\text{SiCl}_3$) for various immersion periods, resulting in partial coverages between 42% and 88% of a complete monolayer. Preadsorption of a partial monolayer of OTS was found to drastically improve the molecular alignment of subsequently adsorbed AHTMS. This effect was observed for submonolayer OTS films exhibiting both an island or a homogeneous growth mode, as determined by atomic force microscopy. Without preadsorbed OTS, the adsorption of AHTMS from an aged solution typically resulted in films of multilayer thickness, while the use of fresh solutions of AHTMS resulted in disordered films of submonolayer coverage. We suggest that submonolayer quantities of preadsorbed OTS prevent coagulated aminosilane adsorption and enable oriented adsorption of aminosilane molecules along the domain perimeter of aligned and ordered methyl-terminated silane. In comparison to sequential adsorption, coadsorption of *n*-octadecyltrimethoxysilane (OTMS; $\text{CH}_3(\text{CH}_2)_{17}\text{Si}(\text{OCH}_3)_3$) with AHTMS from a mixture gave films of low quality. The OTS/AHTMS surface that was prepared by sequential adsorption was exposed to pentafluorobenzaldehyde (PFBA) to probe the reactivity and orientation of the AHTMS amino groups. Eighteen to thirty-four percent of the amino groups reacted with no or minor disturbance to the molecular order, compared to 21–44% on pure and disordered AHTMS multilayers. This indicates that the coupling reaction with PFBA in toluene involves only part of the amino groups at the interface.

Introduction

It is well-known that *n*-octadecyltrichlorosilane (OTS) forms self-assembled highly ordered monolayers on a variety of substrates.^{1–5} Due to a lack of reactive tail groups, OTS cannot be used for covalent coupling reactions, e.g., reaction with an aldehyde for antibody immobilization in biosensor applications.⁶ Long alkyl chain (17-aminoheptadecyl)trimethoxysilane (AHTMS) aminosilane films have the desired functionality for further reactions and were investigated in terms of their molecular order, film thickness, and composition.⁷ We found, however, that AHTMS aminosilane films having the same alkyl chain length as OTS show no preferential molecular orientation with respect to the substrate surface. This is presumably caused by chemical interactions between amino and silanol groups, as inferred from X-ray photoelectron spectroscopy (XPS) and infrared (IR) spectroscopy

measurements,^{7,8} which gives evidence for the presence of free, hydrogen-bonded, and protonated amino groups in the films.

In this paper we report results showing that a preferential molecular orientation of AHTMS molecules can be achieved by templating to preadsorbed OTS. Coadsorption of OTS and long chain substituted cyanine dyes was the first method employed to investigate the orientation of the alkyl chains in the film.⁹ Voids in the OTS films due to solvent retention of hexadecane and its release by rinsing with chloroform could be filled in with octadecanamine and octadecanoic acid¹⁰ or with OTS itself.¹¹ Dilution with the corresponding methyl-terminated trichlorosilanes or backfilling was found to solidify mixed monolayers with a long chain 2-naphthyl-tagged *n*-alkyltrichlorosilane.¹²

The concept of using lateral templating to induce orientational order in otherwise disordered systems came from our previously reported observation that OTS forms islands in the submonolayer coverage range with a high preferential molecular order.^{7,15} Supported by our recent Monte Carlo calculation on the phase behavior in self-assembling alkane monolayers,¹³ this can be explained

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[†] This paper is dedicated to Professor R. Gleiter on the occasion of his 60th birthday.

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by a high lateral mobility of the adsorbed molecules and a two-dimensional condensation of ordered domains, driven by the attractive van der Waals interaction between the alkane chains of ca. 2 kcal/mol per methylene unit. Hence, if the lateral attractive van der Waals interactions between the alkane chains can energetically compensate for the acid/base interactions between the amine groups of AHTMS and the surface silanol groups, a lateral templating leading to oriented AHTMS should be possible.

As will be shown, there exists another important factor besides lateral templating which contributes to ordered monolayer growth, i.e., the inhibition of coagulated AHTMS particle adsorption from solution by preadsorbed OTS. This indicates that partial hydrophobization of the silanol surface protects the surface from coagulated AHTMS and, hence, from multilayer adsorption.

Experimental Section

Sample Preparation. *n*-Octadecyltrichlorosilane, OTS (Merck, >98%), octadecyltrimethoxysilane, OTMS (Fluka, ~90%), pentafluorobenzaldehyde, PFBA (Aldrich, 98%), and bicyclohexyl (Fluka, >99%) were used as received. The synthesis of (17-aminoheptadecyl)trimethoxysilane (AHTMS) has been described previously.¹⁴ H₂SO₄, 30% H₂O₂, toluene, and chloroform were of analytical quality.

The substrates of 1.5 cm × 2 cm size were cut from double-sided polished, 0.5 mm thick Si(100) wafers. Prior to film preparation, the substrates were cleaned by a wet chemical treatment in a freshly prepared hot acid mixture (3:1 v/v mixture of H₂SO₄ and 30% H₂O₂ at ~80 °C, *caution: this mixture reacts violently with organic materials and must be handled with great care*) for 1 h followed by an extensive rinse with ultraclean water (Millipore) and blown dry with nitrogen. Film preparation of complete OTS films was performed by immersing the Si substrates for 24 h in a 1 mM OTS solution in bicyclohexyl. The trimethoxysilane (AHTMS and *n*-octadecyltrimethoxysilane, OTMS) films were prepared from a 0.1 M bicyclohexyl solution. To remove excess silane aggregates, the samples were rinsed with Millipore water, stirred in a chloroform bath for several minutes, and blown dry. If there was still some excess polymer visible under a fiber optical illuminator, the samples were wiped with a soft 100% cotton cloth (TX 304, Texwipe Co., Upper Saddle River, NJ) which was dipped in chloroform.

OTS submonolayer films were prepared by preadsorption of OTS for 15, 60, or 120 s, followed by the treatment with Millipore water and chloroform. Afterward, one of the identically treated samples was treated with an AHTMS solution for 24 h, others were examined using AFM, IR spectroscopy, XPS, and near-edge X-ray absorption fine structure spectroscopy (NEXAFS).

Pentafluorobenzaldehyde was used in the form of a 0.1 M solution in toluene. After a 24 h immersion period, the samples were rinsed with water and toluene and wiped with a cotton cloth. For further details of the sample preparation, see refs 7 and 15.

XPS. The XPS experiments were carried out on a Leybold MAX-200 spectrometer using a Mg K α X-ray source operating at 300 W power consumption. The pressure in the XPS system during the measurements was better than 10⁻⁹ mbar. Survey spectra were recorded prior to and after the XPS experiments in order to check for beam damage in the films. No changes due to X-ray exposure could be detected in the survey spectra for the experimental conditions applied. Spectra were recorded in the normal emission mode and were normalized for constant transmission using the software supplied by the manufacturer, and electron binding energies were calibrated against the alkyl C 1s emission peak at $E_b = 284.6$ eV. The attenuation of the Si 2p peak of the substrate silicon was used to determine the average thickness of the adsorbed layers, assuming an electron mean free path of 34 Å.⁷ The attenuation of the substrate signal is different for a film of uniform thickness, as compared to a submonolayer film with island formation. For a uniform film,

Table 1. Mixed OTS/AHTMS Samples

| sample | % preadsorption of OTS normalized to full OTS monolayer (100%) | growth mode | % normalized coverage after subsequent adsorption of AHTMS |
|--------|--|------------------------------------|--|
| A | 88–93 ^{a,b} | OTS islands, ~0.8 μ m diameter | 110 ^a |
| B | 45–54 ^b | OTS islands, ~0.1 μ m diameter | 87 |
| C | 42 | homogeneous | 89 |
| D | 64 | homogeneous | 100 |
| E | 74 | homogeneous | 100 |

^a The data include some physisorbed OTS which was not, but could be, removed by wiping with a cotton cloth. ^b The normalized precoverages were calculated from the attenuation of the XPS Si 2p substrate signal. For the island growth mode submonolayers, the real precoverage is between the lower value calculated for a film of homogeneous thickness and the higher value calculated assuming islands of fully extended OTS chains.

the substrate signal decreases exponentially with the film thickness, while the attenuation is directly proportional to the coverage for an island growth mode. The uniform overlayer gives a somewhat higher attenuation than that of an island film with the same average thickness, as indicated in Table 1. The difference is a function of the electron mean free path through the specific adsorbate and decreases with increasing coverage. Hence, the real average thickness will be within the lower limit calculated for a uniform film and the higher limit for a film with islands of fully extended OTS molecules with their chain axes perpendicular to the surface plane.

C:N:F stoichiometries were calculated from detailed spectra of the corresponding 1s peaks, using relative sensitivity factors of 1:1.77:3.28, as determined for the MAX-200 spectrometer, and a linear background subtraction routine.

FTIR. The normal transmission and Brewster angle IR spectra were taken with a Fourier transform spectrometer (Model IFS-66v, Bruker, Germany) at 4 cm⁻¹ resolution. The resulting interferograms were Fourier transformed with Blackman–Harris 3-term apodization.¹⁶ The point density in the spectra was increased with zero-filling¹⁷ by a factor of 8. All spectra were ratioed against reference spectra of cleaned silicon samples from the same wafer. For complete, ordered monolayers, the discrepancy in the d[±] peak positions between two individual measurements was ca. ± 0.2 cm⁻¹. Spectra of submonolayer and disordered films with weak, broad bands are more sensitive with respect to the slight variations of the spectrometer optics and the cleaning of the silicon samples used for the background spectra. At ~40% coverage, we observed variations of up to ± 1 cm⁻¹ in the band widths and ± 0.5 cm⁻¹ in the peak positions as a consequence of a change of the reference sample.

The transmission of an IR beam through a silicon wafer with two parallel sides causes sinusoidal modulations (fringes) on the base line of the IR spectra. The periodicity of the fringes is inversely proportional to the thickness of the wafer. For the 0.5 mm thick Si wafer used in the present study, the maximum possible resolution for which the fringes are not resolved is limited to about 4 cm⁻¹. Experimentally, the problem of interferences can be solved by wafers with nonparallel sides⁵ or by performing measurements in the Brewster angle (θ_B) configuration,¹⁸ i.e., using a p-polarized IR beam incident to the surface at the Brewster's angle ($\theta_B = 73.7^\circ$ for Si with an index of refraction of 3.42). The latter method offers the advantage that at near-grazing incidence, vibrations perpendicular to the surface will be enhanced relative to vibrations parallel to the surface. Thus, the dichroic ratio $A(\theta_B)/A(0^\circ)$ for each absorption band is a measure for the average orientation in the thin organic film. With the sample mounted on a rotary stage, spectra in both configurations can be obtained. In the Brewster angle configuration, we use a p-polarized IR beam with a diameter of about 2 mm, and in normal transmission, the KRS-5 wire grid polarizer is removed.

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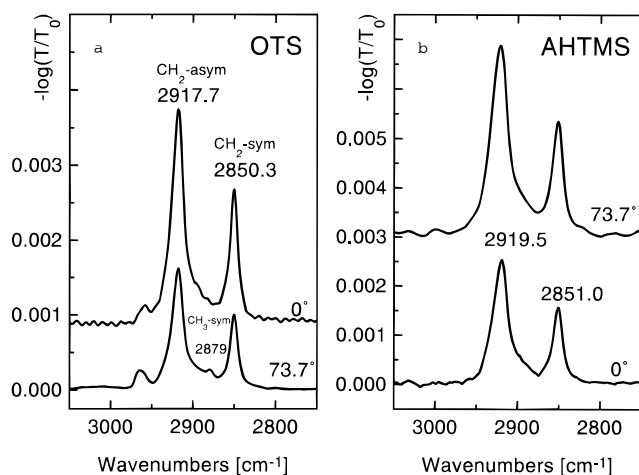


Figure 1. IR spectra of (a) a complete OTS monolayer and (b) a AHTMS film of about bilayer thickness in the normal transmission (0°) and Brewster angle configuration (73.7°). For OTS, the reduction of the methylene bands at 2917 and 2850 cm^{-1} as well as the increase of the CH_3 sym band at 2877 cm^{-1} , when going from normal to glancing transmission, indicate an ordered film. AHTMS methylene peak positions of 2919.6 and 2850.9 cm^{-1} indicate a reduced but still partly existing molecular alignment, while dichroic ratios in a range from 1.1 to 1.6 indicate an average tilt angle of about 38 – 51° .

Normal transmission and Brewster's angle transmission spectra of monolayer OTS films gave peak positions of 2917.7 cm^{-1} for the methylene C–H antisymmetric (d^-) mode and 2850.3 cm^{-1} for the symmetric (d^+) mode, as shown in Figure 1a. These values are within the range of the peak positions reported previously by others^{2,3,19} and are interpreted as characteristic for all-trans alkyl chains in a crystalline-like phase. Despite an increase in the optical pathway when going from normal to glancing transmission, the band heights of both of the methylene stretching modes decrease to about 55% of their height in normal transmission. Note also the presence of the CH_3 symmetric mode at 2879 cm^{-1} in glancing transmission. This band is hardly visible in normal transmission spectra, as expected for a vibrational mode with an essentially perpendicular orientation to the surface plane.

For a quantitative interpretation of the dichroic ratios, we simulated the data with a matrix method described by Parikh and Allara.²⁰ With this method, the optical properties of the organic film are derived from the bulk spectra of a suitable model compound. For the simulation of a crystalline-like ordered C_{18} film, we chose the bulk spectrum of crystalline *n*-octadecyl disulfide²¹ as an isotropic reference for an all-trans alkane chain with 17 methylene units. This method has been used previously for a quantitative interpretation of OTS film spectra on silicon surfaces in external reflection geometry.²² We do not claim that the bulk spectra of a long alkyl disulfide is a valid reference spectra for the methylene absorption bands of submonolayers of OTS and AHTMS samples because a set of different monofunctional long alkyl chain molecules shows differences in band widths and intensities.⁵ The ratio of the IR band intensities in glancing and normal transmission, that we use for a calculation of the average tilt angle, is less affected by such variations in band widths and band intensities. Note that the dichroic ratios for the antisymmetric and the symmetric methylene stretching mode are nearly identical.

The twist angle, which effects the ratio between the symmetric and antisymmetric methylene stretching bands for any non-normal orientation, was fixed at 45° . Hence, in agreement with the experimental results, the angle between the transition moment and the surface normal was always identical for both the symmetric and antisymmetric vibrations.

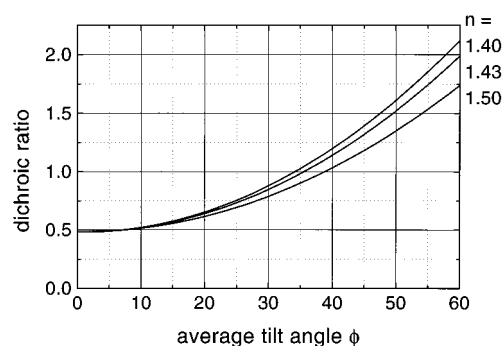


Figure 2. Dichroic ratio, i.e., band height for CH_2 asym in the Brewster angle configuration divided by the band height in the normal transmission configuration, as calculated from spectra simulations as a function of the tilt angle ϕ between the chain axis and the surface normal for a refractive index of 1.40, 1.43, and 1.50.

The real part of each complex tensor element of the organic layer was obtained by an appropriate Kramers–Kronig transformation, assuming a refractive index of 1.43 in the nonabsorbing regions as it was found for pure liquid and crystalline paraffins.²³ Because the matrix method takes into account multiple reflections at the front and back Si–air interface, the spectra simulations show sinusoidal modulations when the thickness of the substrate is a multiple of $\lambda/2$ in the respective medium. To eliminate interference fringes from our calculations, we used the reflectance (r) and transmittance (t) coefficients that were calculated with the matrix method for an air–Si and Si–air interface in combination with the classical formula describing the fraction of power transmitted (T) when there is no coherence between the two interfaces.

$$T = |t_{13}|^2 \cdot |t_{31}|^2 + |t_{13}|^2 \cdot |r_{31}|^4 \cdot |t_{31}|^2 + |t_{13}|^2 \cdot |r_{31}|^8 \cdot |t_{31}|^2 + \dots = \frac{|t_{13}|^2 \cdot |t_{31}|^2}{1 - |r_{31}|^4}$$

Calculating the coefficients t_{13} , t_{31} , and r_{31} in the presence of the organic film (medium 2) and for the film-free interface resulted in fringe-free spectra simulations without ignoring the contribution of the multiple internal reflections to the absorbance spectra in normal transmission. As a result, spectra simulations for a 26 Å thick layer of oriented alkane chains in normal transmission and in the Brewster angle configuration resulted in the relationship of the dichroic ratio of the methylene C–H antisymmetric stretching band and the molecular tilt angle ϕ shown in Figure 2. The dichroic ratio $A(73.7^\circ)/A(0^\circ)$ for the d^- mode of 0.55 for OTS monolayers corresponds to an average tilt angle, ϕ , of 13° , in good agreement with earlier findings of 10 – 18° ,³ 0 – 10° ,⁷ 8° ,²² and 11° .⁵

No correction was made for the experimental angular spread of $\pm 5^\circ$ of the angle of incidence because the deviations from the Brewster angle were symmetric, so that the deviation for an angle of incidence greater than that calculated will mainly be compensated for by the deviation caused by a smaller angle of incidence.

NEXAFS. The NEXAFS spectra were recorded at the synchrotron radiation facility BESSY in Berlin using a HE-TGM 2 monochromator. For the experimental details and a brief description of the method, see ref 7. X-ray absorption spectra at the C 1s edge are dominated by a C 1s \rightarrow Rydberg states (R) resonance at 287.7 eV and a C 1s $\rightarrow \sigma^*$ resonance at 293 eV. The C 1s $\rightarrow \sigma^*$ resonance is polarized along the molecular axis of OTS, and the transition dipole moment of the C 1s \rightarrow R resonance is orthogonal to the C 1s $\rightarrow \sigma^*$ transition dipole.²⁴ From the variation of these two resonances with the angle of incidence, θ , of the photons, the average orientation of the electronic transitions

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can be calculated within the dipole approximation and interpreted with a model of uniformly tilted all-trans alkyl chains.

AFM. The OTS growth behavior (island or homogeneous growth mode) was investigated under ambient conditions with a Park Scientific Autoprobe CP system with a 5 μm scanner. Constant force images were taken in the repulsive mode with a silicon nitride cantilever having an integrated pyramidal tip. Typical forces were on the order of 10 nN, using a 200 μm long cantilever with a spring constant of 0.06 N/m.

Results

Neat AHTMS Films. The properties of neat AHTMS films were not found to be reproducible in a quantitative sense; they exhibit strong variations with age and appearance of the AHTMS solution from charge to charge. The presence of the nucleophilic amine group in the molecule promotes the polymerization of the alkoxy silane in solution. Thus, both surface reaction and polymerization in solution occur simultaneously during immersion of the sample.²⁵ A clear AHTMS solution in bicyclohexyl resulted in films with submonolayer to monolayer coverage. IR spectra of these submonolayer AHTMS films show d^- and d^+ mode peaks at 2924 and 2854 cm^{-1} , respectively, values which approach those that are associated with highly conformationally disordered chain assemblies.²⁶

Adsorption from an initially cloudy solution always resulted in coverages exceeding one monolayer. Physisorption of polymerized silane molecules was also observed for OTS films, but excess adsorption could be completely removed by wiping with a cotton cloth. Contrary, in the case of AHTMS, polycondensate adsorption was resistant to extensive water and chloroform rinsing and wiping. In comparison to AHTMS submonolayer films, the methylene stretching modes in the AHTMS multilayer film spectra were significantly shifted to lower wavenumbers. The measured absorption maxima, in normal transmission, in the range from 2919 to 2920 cm^{-1} and about 2851 cm^{-1} show that the average chain conformation is neither all-trans nor liquid-like disordered. Note that opposite to the behavior of complete OTS films, the absorption bands increased when going from normal to glancing transmission (Figure 1b). Because the thickness of the neat AHTMS multilayer films was not constant over the whole sample and the IR beam spot size was not the same for normal ($\sim 3 \text{ mm}^2$) and glancing transmission ($\sim 11 \text{ mm}^2$), different measurements for the dichroic ratio were scattered in a broad range from 1.1 to 1.6. Interpretation with the optical function of *n*-octadecyl disulfide results in tilt angles between 38° and 51°, consistent with an almost random orientation. NEXAFS spectra (Figure 3) of neat AHTMS films, in contrast to spectra of neat OTS films, did not vary with the angle of incidence,⁷ corresponding to either a uniform tilt angle near the magic angle of 54.7° or a random distribution of the transition dipole moments.

In the lower wavenumber range, the IR spectrum (Figure 4) of a neat AHTMS film (thickness ca. 50 Å) shows two strong bands at 1636 and 1540 cm^{-1} besides the methylene scissoring band at 1467 cm^{-1} . Broad bands at 1640 and 1568 cm^{-1} were also found²⁷ in the spectra of physisorbed multilayers of (3-aminopropyl)triethoxysilane on Au after exposure to ambient conditions and were assigned to ammonium bicarbonate formation, and we propose the same assignments of the bands at 1636 and 1540 cm^{-1} in our experiments.

The XPS spectra of the N 1s region of neat AHTMS films (Figure 5) show an asymmetric broad band, which

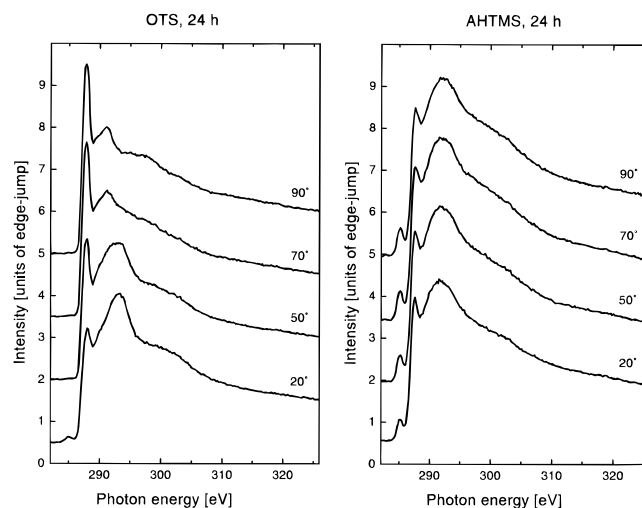


Figure 3. Series of NEXAFS spectra for OTS (left) and AHTMS (right) for different angles of incidence ranging from 20 to 90°.

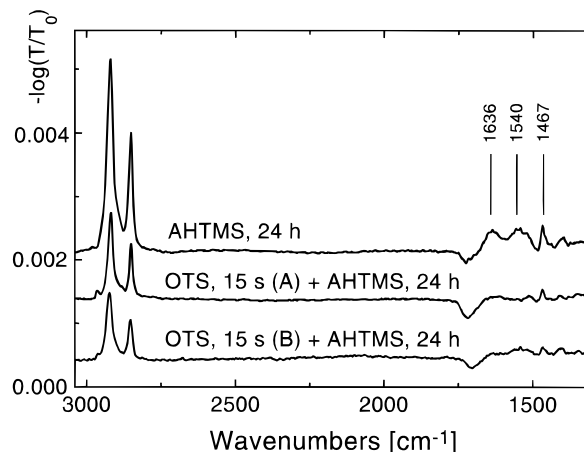


Figure 4. Glancing transmission spectra showing the region between 3000 and 1300 cm^{-1} of a neat AHTMS sample (upper curve) and the two OTS/AHTMS films A and B (Table 1). Negative absorption bands at ca. 1720 cm^{-1} are due to a self-cleaning effect of the adsorption process reducing the amount of carbonic acid and ester contaminations on the silicon surface.

can be fit by a peak ascribed to the NH_3^+ species with a binding energy of ca. 402 eV²⁸ and two peaks ascribed to hydrogen bonded and free NH_2 groups at 400–401 and 399 eV, respectively.¹⁰

Both CO_2 dissolved in H_2O ($\text{p}K_a$ 6.35)²⁹ and the surface SiOH groups ($\text{p}K_a \sim 7.1$)³⁰ are acidic enough to protonate the amine group (the $\text{p}K_a$ of a long alkyl chain ammonium group is ~ 10 –11).³¹ The Si-OH groups of hydrolyzed, but not polymerized, silane head groups are about 4 orders of magnitude less acidic than surface silanol groups and associate via hydrogen bonds. The relative amount of the different species that were observed in the XPS spectra was determined with a peak fitting routine assuming Gaussian peak shapes with predetermined peak positions (401.8, 400.3, and 399.3 eV) and halfwidths of 1.6 eV. For two samples with bilayer thickness (Figure 5a,b), prepared from the same AHTMS stock solution, the percentage of the protonated nitrogen species was about

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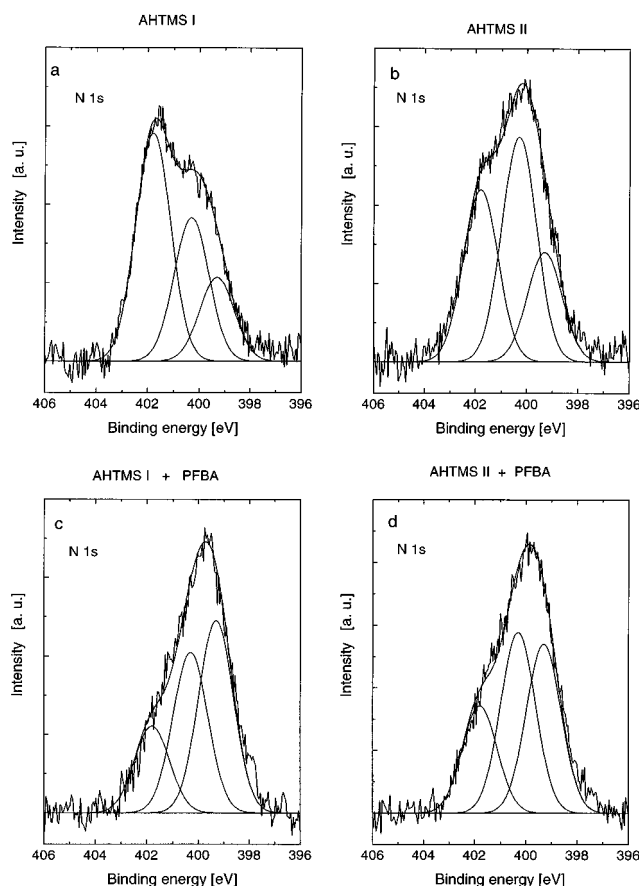


Figure 5. XPS N 1s single scans of two neat AHTMS films, prepared from the same stock solution, with a percentage of protonated nitrogen species at $E_b \sim 401.8$ eV of (a) 34% and (b) 50%, and (c, d) N 1s scans of the same samples after coupling with pentafluorobenzaldehyde.

35% and 50% of the total nitrogen content. For sample AHTMS I of Figure 5a, the larger concentration of the NH_3^+ species is correlated with a reduced amount of hydrogen bonded amino groups (ca. 30% for sample I and ca. 45% for sample II). The percentage of free amino groups for both samples was about 20%.

AHTMS Adsorption onto OTS Precovered Substrates. As previously reported, the properties of OTS submonolayers prepared in a chemistry laboratory atmosphere are different from the properties of samples prepared under clean room conditions. Reproducible results, with respect to the growth mode, could only be obtained in a clean room atmosphere. AFM images of OTS submonolayers prepared under clean room conditions (class 100, 21 °C, 45% atmospheric humidity) reveal an island growth mode for the film.¹⁵ The islands are branched with typical diameters of 0.6–0.9 μm and heights of $h = 25.4 \pm 2.5$ Å. With the exception of sample A, all of the other OTS submonolayers used in the present study were prepared in a normal chemistry laboratory. This leads to a different island size distribution. In some of the chemistry laboratory prepared series the sizes of the islands were found to be reduced to about 0.05–0.2 μm , while other series showed no OTS island at all in the AFM measurements. We refer to the latter as the “homogeneous” growth mode. The growth mode (AFM) and the average film thickness (XPS) before and after subsequent adsorption of AHTMS for the five different approaches used in the present study are summarized in Table 1.

The film thickness of 110% (normalized to a complete OTS monolayer) and 30 Å for sample A, after subsequent

adsorption of AHTMS, exceeds the theoretical thickness of ~ 26 Å for a monolayer with perpendicularly oriented all-trans OTS/AHTMS alkane chains. This was obviously due to excess adsorption of physisorbed silane, which was subsequently removed by the immersion in PFBA/toluene and the treatment with a cotton cloth and solvent rinsings. Wiping of submonolayer OTS or AHTMS films with a cotton cloth was avoided because cotton fibers contain fatty acids (so-called cotton wax³²) that might be extracted by organic solvents and strongly adsorb on high-energy surfaces.

We examined different procedures to calculate the OTS:AHTMS stoichiometry from the XPS data: Using the ratio of the film thicknesses before and after subsequent adsorption of AHTMS, as determined by the attenuation of the Si 2p peak, resulted in ratios for OTS:AHTMS of 5:1 (A) and 1:1 (C). However, the added material does not show the expected C:N ratio of 17:1 but exhibits an excess of carbon with a ratio of 25:1. The same problem was also found for neat AHTMS films, for which the ratio is also 25:1, similar to the case of short chain aminosilanes where the surplus of carbon was even higher.³³ The minimum time that was required for a precise determination of the N 1s intensity was about 20 min, and we found no indication of X-ray beam damage during this time. Hence, we suggest that the organic contaminations that were adsorbed from solution or the ambient conditions during transfer onto the polar aminosilane surface are the most probable cause for the C 1s surplus. Consequently, the calculation of the OTS:AHTMS ratio from the C:N ratio of the mixed OTS/AHTMS film yields a lower percentage of AHTMS, between 20% (A) and 40% (C), as compared with the estimate based on changes in film thickness. We exclude a displacement of pre-adsorbed OTS by AHTMS because we observed no AHTMS adsorption into complete OTS films and no desorption of complete OTS films or OTS submonolayers after repeated solvent rinsings.

Figure 6 shows the CH stretching bands of preadsorbed OTS (left) and the corresponding data for the OTS/AHTMS films (right). The peak positions and halfwidths of both the antisymmetric and symmetric methylene stretching modes are summarized in Table 2. Normal transmission spectra yield more reliable values for the peak positions and fwhm because the anomalous dispersion influences band positions and shapes more in glancing transmission. In the case of the homogeneous growth mode films C, D, and E, there is a lower limit of about 50% coverage. Below that level there is a liquid-like disorder as indicated by d^\pm frequencies of 2923.5 and 2855.2 cm^{-1} and a dichroic ratio of ~ 1.6 , which corresponds to an average tilt angle of $\sim 52^\circ$. The band positions were shifted by AHTMS adsorption to 2921.2 and 2851.8 cm^{-1} , and the dichroic ratio decreased to ~ 0.91 , corresponding to a tilt angle of 32° . The other two samples of this series with a homogenous OTS precoverage of 64% (D) and 74% (E) already show, before addition of AHTMS, peak positions which indicate a partial stretching of the alkyl chains. For these samples, the d^- band positions of 2920.4 and 2919.5 cm^{-1} , respectively, remain, within experimental error, unchanged even after addition of AHTMS. The same applies to the dichroic ratio of 0.84 and 0.66, respectively, which corresponds to an average tilt angle of $\sim 30^\circ$ and 21° , respectively.

For samples A and B, it is problematic to calculate the average tilt angle from the dichroism of the methylene stretching modes because, in the case of island growth

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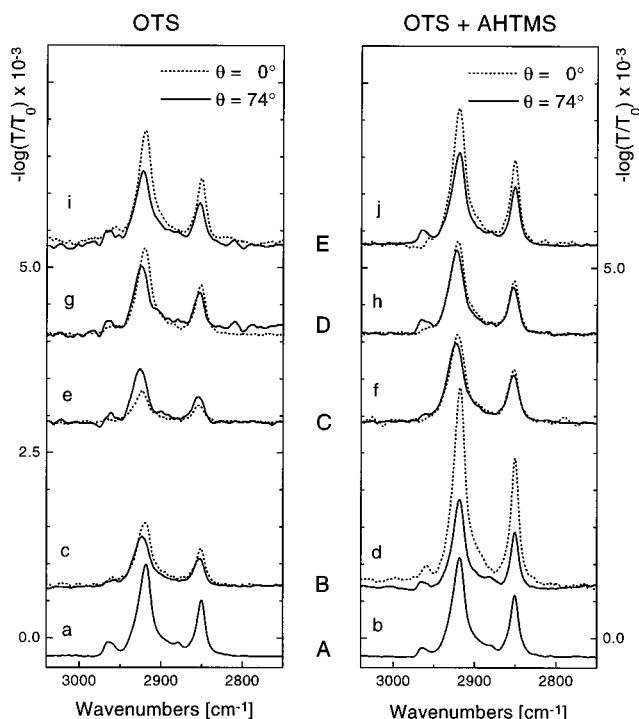


Figure 6. Transmission spectra of preadsorbed OTS submonolayer films (left) and the corresponding OTS/AHTMS films (right) in normal (dotted curve) and glancing transmission configurations (straight curve).

mode, there might be significant deviations from the assumed refractive index of 1.4–1.5. In the island model, the index of refraction is a monotonic function of the coverage, varying from 1 at zero coverage to the monolayer value at complete coverage. The identical methylene stretching peak maxima in the case of sample A and the decrease in the band positions and halfwidths in the case of sample B, however, indicate an ordering effect of the preadsorbed OTS. For the resulting mixed OTS/AHTMS samples A and B, the peak positions at 2918 cm^{-1} and lower indicate that the percentage of gauche conformations is within the range usually ascribed to crystalline-ordered films. The samples of the homogeneous growth mode series do not approach that range of ordering, as indicated by the vibrational frequencies.

For mixed OTS/AHTMS sample B, the IR dichroism of 0.45 is even better than for a complete OTS film (0.55) and indicates a more dense packing of the alkane chains and a lower amount of defects for the mixed film. The dichroic ratios indicate as well that despite the resulting

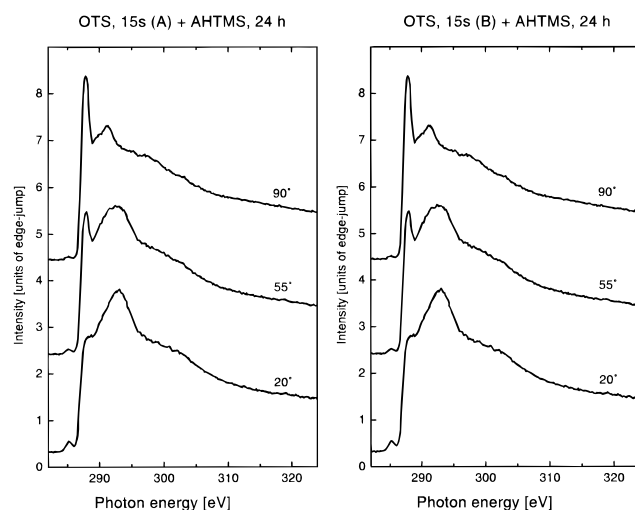


Figure 7. Series of NEXAFS spectra of mixed OTS/AHTMS films prepared by adsorption of AHTMS onto island growth OTS submonolayers A and B.

same OTS:AHTMS stoichiometry, the degree of orientation is lower for the adsorption onto a homogeneous OTS submonolayer (C) than for the adsorption onto an already ordered, island growth submonolayer (B).

The NEXAFS spectra are in qualitative agreement with the IR data and reveal a maximum dichroism for the mixed OTS/AHTMS sample B (Figure 7) and an increase of the dichroism for the homogeneous growth mode series after the sequential adsorption of AHTMS (Figure 8). The data are summarized in Table 2.

The spectral range between 3000 and 1300 cm^{-1} for two OTS/AHTMS films is compared with the spectrum of a neat AHTMS film in Figure 4. Bicarbonate salt bands at 1636 and 1540 cm^{-1} are too weak to be detected in the OTS/AHTMS spectra. The XPS N 1s single-scan spectra (Figure 9a,b) reveal that there is 25–30% of the protonated nitrogen species and ca. 25% of free amino groups in the mixed OTS/AHTMS films. Hence, the percentage of the protonated nitrogen species in mixed OTS/AHTMS films is lower than that in neat AHTMS films of about bilayer thickness.

Coadsorption of AHTMS with OTMS. In addition to subsequent AHTMS adsorption into the voids of submonolayer OTS films, we also investigated the simultaneous adsorption of AHTMS and long chain *n*-octadecyltrimethoxysilane (OTMS). The IR data (Figure 10) of a complete (24 h immersion time) OTMS film revealed that the film quality was similar to that of the corre-

Table 2. IR Methylene Stretching Band Positions and Halfwidths of Samples A–E with and without Subsequent Adsorption of AHTMS, and Average Chain Orientations Determined with IR and NEXAFS Spectroscopy

| sample | figure | $d^- \text{ cm}^{-1}$ | | $d^+ \text{ cm}^{-1}$ | | dichroic ratio ^a | av tilt angle (deg) | |
|---------|--------|-----------------------|-------------------|-----------------------|-------------------|-----------------------------|---------------------|-----------------|
| | | peak max | fwhm | peak max | fwhm | | IR | NEXAFS |
| A | 6a | 2918.2 ^b | 17.6 ^b | 2850.2 ^b | 11.2 ^b | | | |
| + AHTMS | 6b | 2918.1 ^b | 17.7 ^b | 2850.3 ^b | 11.4 ^b | | | |
| B | 6c | 2919.0 | 20.5 | 2851.1 | 12.2 | 0.78 | 27 | 39 |
| + AHTMS | 6d | 2917.7 | 16.1 | 2850.2 | 10.8 | 0.45 | 0 | 20 |
| C | 6e | 2923.5 | 21.4 | 2855.2 | 18.0 | 1.62 | 52 | 54 ^b |
| + AHTMS | 6f | 2921.2 | 21.6 | 2851.8 | 14.4 | 0.91 | 32 | 43 |
| D | 6g | 2920.4 | 18.9 | 2851.5 | 13.5 | 0.84 | 29 | 49 |
| + AHTMS | 6h | 2920.7 | 20.1 | 2851.7 | 13.0 | 0.89 | 31 | 33 |
| E | 6i | 2919.5 | 17.6 | 2850.7 | 11.8 | 0.66 | 21 | 48 |
| + AHTMS | 6j | 2919.1 | 18.5 | 2850.7 | 11.8 | 0.66 | 21 | 38 |
| OTS | 1a | 2917.7 | 16.0 | 2850.3 | 10.6 | 0.55 | 13 | 0–10 |
| AHTMS | 2 | ≥2918.7 | ≥19.0 | ≥2850.6 | ≥12.3 | 1.1–1.6 | 38–51 | 54 ^b |

^a IR d^- band height at glancing incidence ($\theta_B = 73.7^\circ$) divided by the band height in normal transmission ($\theta_B = 0^\circ$). ^b Values are for glancing incidence. No spectra in normal transmission available. ^c Average tilt angles close to the magic angle of 54.7° can also indicate random molecular tilts, e.g., no orientational order.

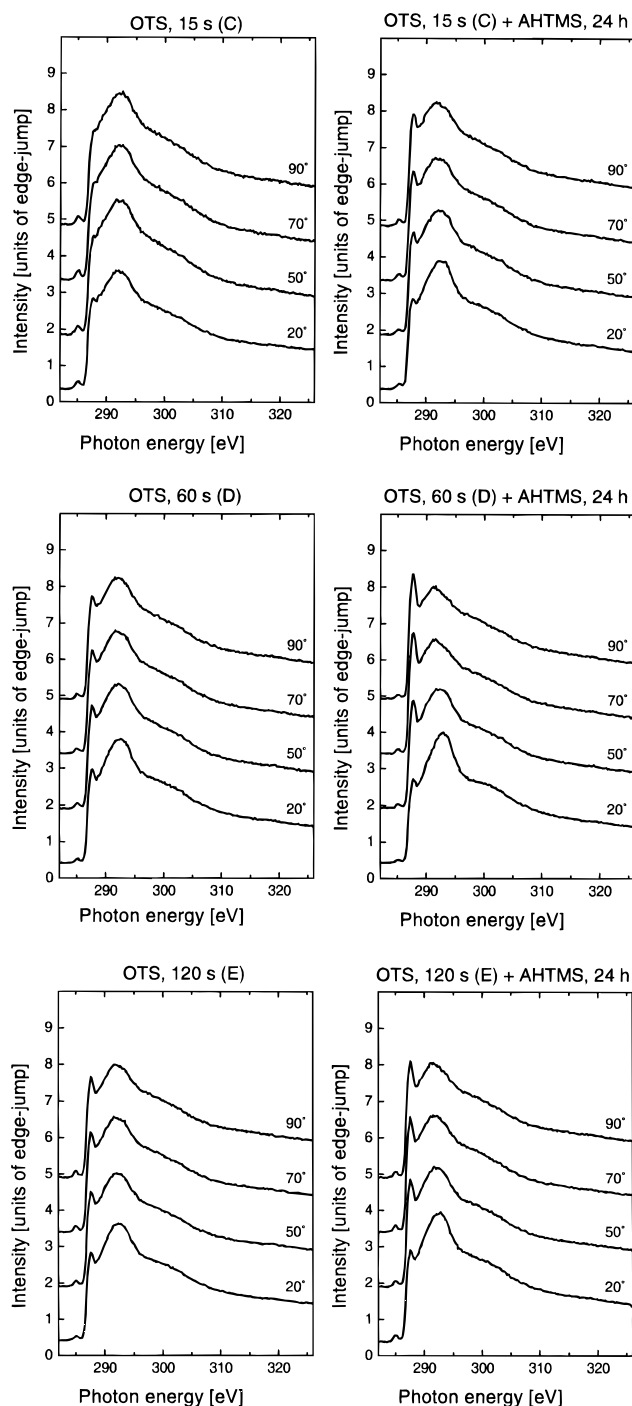


Figure 8. Series of NEXAFS spectra of OTS submonolayers C–E and the corresponding mixed OTS/AHTMS films.

sponding trichlorosilane films. The d^{\pm} mode peaks of 2917.5 and 2850.1 cm^{-1} , in combination with the appearance of the CH_3 symmetric mode band in glancing transmission, strongly suggest that OTMS monolayers dominantly consist of all-trans extended chains. Mixed monolayers were prepared by coadsorption from 1:1 and 1:3 v/v mixtures of AHTMS and OTMS at a constant total concentration of 0.1 M in bicyclohexyl. Adsorption from the equimolar solution resulted in a ca. 32 Å thick film of mainly ($\sim 77\%$) AHTMS, as determined by XPS. Similar to the findings for neat AHTMS films, the IR peak positions of 2920.4 and 2851 cm^{-1} revealed a conformational order, despite a dichroic ratio of 1.2, corresponding to an average tilt angle of ca. 40°. The sample that was prepared from the 1:3 AHTMS/OTMS solution resulted in a disordered submonolayer (ca. 20 Å), as indicated by XPS and d^{\pm}

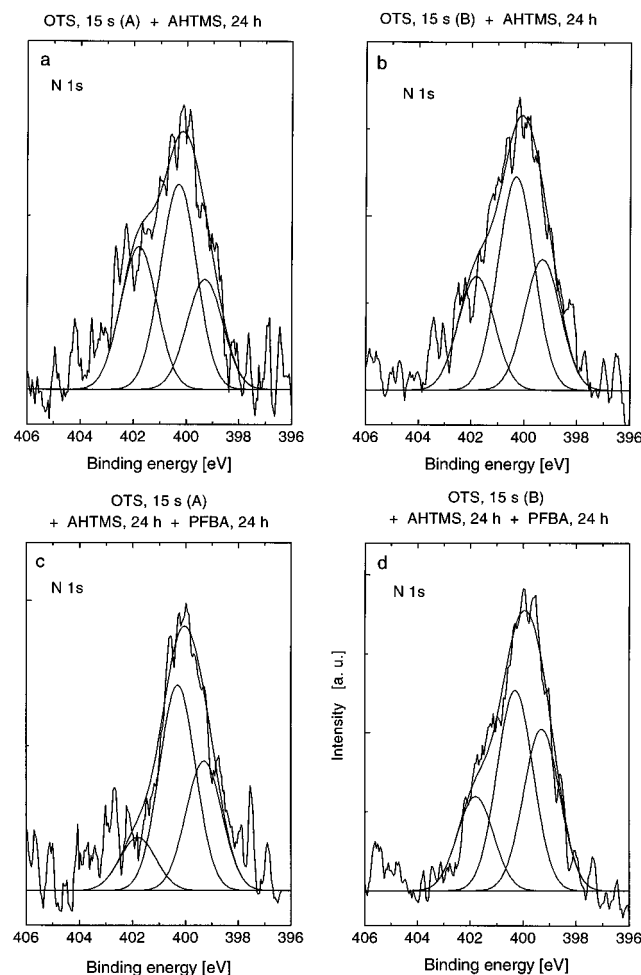


Figure 9. XPS N 1s single scans of two mixed OTS/AHTMS films (a, b) before and (c, d) after coupling with pentafluorobenzaldehyde.

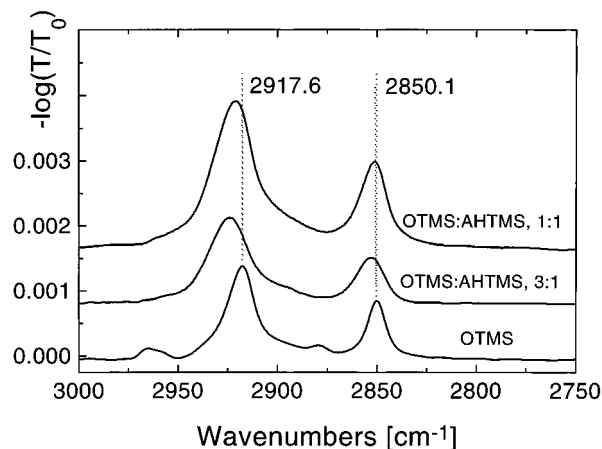


Figure 10. Glancing transmission spectra of a pure OTMS film and AHTMS coadsorbed with OTMS. The dotted line indicates the d^+ and d^- mode peaks of the pure OTMS film.

mode peaks of ca. 2921.5 and 2852 cm^{-1} , and showed a surplus ($\sim 70\%$) of AHTMS.

Coupling with Pentafluorobenzaldehyde. The coupling of AHTMS films with pentafluorobenzaldehyde was studied conveniently by XPS, since fluorine is only contained in the aldehyde (Figure 11). Nitrogen/fluorine XPS intensity ratios for three neat AHTMS films with thicknesses of 39, 45, and 53 Å revealed reaction rates of 21%, 34%, and 44% for the coupling reaction with pentafluorobenzaldehyde, respectively. Comparison of N 1s single-scan spectra of neat AHTMS films before and

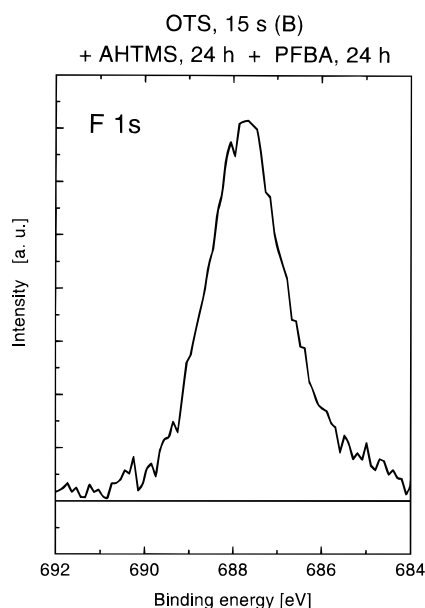


Figure 11. Single-scan XPS spectrum of the F 1s region of a mixed OTS/AHTMS film after a 24 h immersion time in a 0.1 M solution of pentafluorobenzaldehyde in toluene.

after the coupling reaction (Figure 5) shows a decrease of the protonated nitrogen species from 35% to 50% to a constant level of 20–25%. The N 1s signal of the imine nitrogen, usually observed³⁴ at $E_b \sim 399.0$ eV, overlaps with the emission of the free amine group and, hence, does not result in a new peak at a different binding energy in the spectra. The intensity of the low-binding energy imine and the free amine component increases to about 40% of the overall N 1s intensity, as compared to about 20% before the coupling reaction.

The IR and NEXAFS data (Table 3) of neat AHTMS films indicate no improvement in the molecular orientation of the alkyl chains as a consequence of the coupling reaction. As before, the band height of the IR methylene stretching modes increases by a factor of approximately 1.6 when going from normal to glancing transmission, and the NEXAFS spectra show no angular dependence, which is in accordance with a uniform tilt angle of 54.7° or a random distribution of the alkyl chain orientations. A blue shift of the IR d^\pm modes of 2–3 wavenumbers indicates, rather, that the amount of gauche conformations was significantly increased by coupling with PFBA.

Coupling reactions with mixed OTS/AHTMS samples showed (Figure 9) a turnover of 18% (sample A) and 34% (sample B) and a relative increase of the low-binding energy imine and free amine component at 399.3 eV at the expense of the protonated nitrogen species, as observed for the reaction of PFBA with neat AHTMS films. Compared with the XPS spectra taken before the coupling reaction, the XPS spectra of sample A after reaction revealed not only the additional F 1s signal but also a loss of C 1s intensity by about 25%, whereas the relative N 1s intensity increased. Before the coupling reaction, the mixed OTS/AHTMS film was thicker than a neat OTS monolayer (Table 1). Exposure for 24 h in PFBA/toluene, followed by rinsing with water and toluene and the wiping with a cotton cloth, seems to have removed physisorbed OTS, present before the adsorption of AHTMS. Reduced IR d^\pm halfwidths of the methylene stretching modes for sample A after the coupling reaction (Table 2 and 3) are

also in agreement with the assumption of an additional removal of excess disordered adsorption. For sample B, the higher rate was combined with a slight blue shift and an increase in the halfwidths but not with a decrease in film thickness.

After the coupling reaction, the IR dichroic ratio for mixed OTS/AHTMS films was 0.52 (A) and 0.47 (B) (Figure 12). Despite this high orientation (average tilt angles calculated from these values are $<10^\circ$), the glancing transmission spectra of sample B show almost no CH_3 symmetric mode band of OTS at 2878 cm^{-1} , while this band was clearly visible before the coupling (Figure 6d). NEXAFS spectra, only taken for sample B, show only a weak dichroism (Figure 13). A quantitative analysis yields an average tilt angle of 48° . In view of the surface sensitivity³⁵ of the NEXAFS method, which probes only the uppermost ~ 1.5 nm of the organic film, this discrepancy between the IR and NEXAFS dichroism might indicate that the coupling reaction preferentially reduces the chain orientation at the film–vacuum interface.

Discussion

Both NEXAFS and IR spectroscopy give complementary information about the structure of thin organic adsorbates. NEXAFS does not have the problems with the anomalous dispersion as IR spectroscopy does and gives direct information about the orientation of the outermost methylene units. IR spectroscopy, on the other hand, measures the whole film with the same sensitivity and gives information about the average orientation (dichroism) as well as about the average conformation (peak positions). In addition, IR spectroscopy in glancing transmission gives information on the methyl group orientation.

For neat AHTMS films, both methods are in agreement that there is no molecular orientation with respect to the surface normal. The alternative of a uniform tilt angle of approximately 54° is very unlikely. Causes for the missing molecular orientation of neat AHTMS films are interactions between the amino group and the surface silanols. Molecules which are attached by both the silane head group and the amino end group prevent an orientation of the subsequently adsorbed molecules. The same does not apply to multilayer films as indicated by IR spectra showing d^\pm peak frequencies of <2919 and $<2851\text{ cm}^{-1}$, close to the range of values reported for OTS films. There must be some molecular alignment within the multilayer, contrary to physisorption of the agglomerates already polymerized in solution, which results in isotropic films, but this requires further studies.

Both preadsorption of an already aligned OTS island growth mode submonolayer and preadsorption of a liquid-like disordered submonolayer were found to result in oriented, mixed OTS/AHTMS films. Better results, however, were achieved with preadsorption of OTS islands.

In a chemistry laboratory environment, the island growth mode is only observed occasionally. The variations in the growth mode of OTS films are likely due to airborne contaminations. Variations were only seen when different sample series were compared; within one sample series the results were quite consistent. The two-dimensional crystallization that leads to a solid condensed island phase might be hindered by minute quantities of surface active species, such as carbonic acids, alcohols, etc., that are always present in a chemistry laboratory environment. Despite the differences in growth kinetics, all OTS sample preparations, after immersion times of 24 h, resulted in

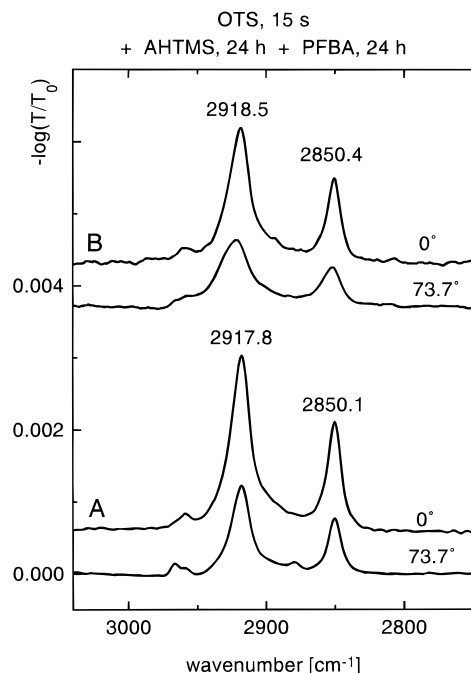
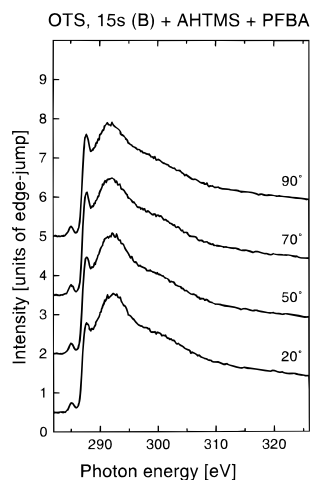
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Table 3. IR Methylene Stretching Band Positions, Halfwidths, and Average Chain Orientations of OTS:AHTMS and Neat AHTMS Samples after Coupling with PFBA

| sample | figure | d ⁻ cm ⁻¹ | | d ⁺ cm ⁻¹ | | dichroic ratio ^a | av tilt angle (deg) | |
|--------|--------|---------------------------------|------|---------------------------------|------|-----------------------------|---------------------|-----------------|
| | | peak max | fwhm | peak max | fwhm | | IR | NEXAFS |
| A | 12a | 2917.8 | 15.8 | 2850.1 | 10.9 | 0.52 | <10 | |
| B | 12b | 2918.5 | 17.5 | 2850.4 | 10.8 | 0.47 | 0 | 48 |
| AHTMS | | 2922.5 | 24.0 | 2852.5 | 15.7 | 2.0 | 60 | 54 ^b |

^a IR d⁻ band height at glancing incidence ($\theta_B = 73.7^\circ$) divided by the band height in normal transmission ($\theta_B = 0^\circ$). ^b Average tilt angles close to the magic angle of 54.7° can also indicate random molecular tilts, e.g., no orientational order.

**Figure 12.** Normal and glancing transmission spectra showing the two 15 s OTS/ 24 h AHTMS samples A and B after coupling with pentafluorobenzaldehyde.**Figure 13.** Series of NEXAFS spectra of the mixed OTS/AHTMS sample B after coupling with pentafluorobenzaldehyde. complete monolayers with an advancing water contact angle of ca. 112° and identical IR spectra.

Fang and Knobler³⁶ showed a homogeneous distribution for the sequential adsorption of perfluorinated *n*-decylsilane onto OTS islands that were prepared by the Langmuir–Blodgett technique as long as the islands were not heated to increase covalent bonding with surface Si–OH groups.

In our experiments, however, we cannot determine the orientation of the AHTMS chains independently of the

orientation of the OTS nor the lateral distribution of OTS and AHTMS and, hence, cannot determine if an island growth mode of the preadsorbed OTS predetermines a phase separation in the mixed OTS/AHTMS films.

Sequential adsorption of OTS and AHTMS, in contrast to the simultaneous adsorption, was found to prevent excess adsorption of coagulated aminosilane. Only single AHTMS chains or smaller aggregates can fit into the voids between the OTS chains. Therefore, the substrate surface is protected from flakes of polymerized aminosilane, and hence, saturation coverage is reached at monolayer thickness. For the homogeneous OTS submonolayers, this is in agreement with previous reports³⁷ that half a monolayer of randomly distributed C₁₈ chains is enough to reduce the reactive area of SiO₂ to $\leq 5\%$. For the island growth mode films, this shielding of the acid surface from AHTMS polymers implies that OTS molecules are adsorbed or physisorbed between the islands, as also concluded from a quantitative comparison between the integral coverage determined by XPS and the monolayer fraction of islands observed in the AFM measurements.

The motivation for our study of the aminosilanes is in its use as a connecting bridge for immobilization of proteins on sensor devices. Long and short alkyl chain aminosilanes readily polymerize in solution. Hence, the film thickness is difficult to control and the surface is a mixture of amine, methylene, methyl, and silanol groups. The covalent immobilization of proteins on these surfaces is usually done by a dialdehyde (e.g., glutardialdehyde) that bridges amino groups of the silane film with amino groups of the protein. Pentafluorobenzaldehyde, PFBA, was used as a model compound for the binding capacity of neat AHTMS and mixed OTS/AHTMS films. For neat AHTMS films, as well as for mixed OTS/AHTMS films, we observe a reduction of the protonated nitrogen species as a consequence of the coupling with PFBA. The lower reactivity of OTS/AHTMS films, as compared to the neat AHTMS films, corresponds to a lower amount of the protonated nitrogen species before as well as after the coupling reaction. The mixing of amino-terminated and methyl-terminated end groups obviously reduces the accessibility of the amino group to CO₂ and H₂O to form carbamate salts but also reduces the ability for the coupling reaction with the aldehyde.

Summary and Conclusions

The thickness of the adsorbed neat AHTMS films was found to depend on the extent of polymerization in the solution. Because this varies strongly with age and water content of the adsorption solution, film properties were not uniform and resulted in coverages ranging from submonolayers to bilayers. With an increasing amount of physisorbed silane, the IR methylene stretching mode frequencies indicated a reduced amount of gauche conformations but no preferential orientation of the chain axes with respect to the surface normal.

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Adsorption of AHTMS into the voids of preadsorbed OTS submonolayer films gave mixed OTS/AHTMS monolayers with a molecular orientation equal or better to that of the neat OTS submonolayer. Hence, it was possible to prepare OTS/AHTMS films with an average tilt angle below 20° and molecular OTS:AHTMS ratios of about 2.3:1.

It was not possible to prepare OTS templates in a reproducible way. The ordering effect for subsequently adsorbed AHTMS was found for both the island growth and homogeneous growth mode films, but the orientation of the island growth mode preadsorbed OTS monolayers before and after subsequent adsorption of AHTMS was better than the orientation of the homogeneous growth mode submonolayers.

Coadsorption from a mixture of amino- and methyl-terminated silanes resulted in less ordered films and did not prevent multilayer adsorption. Hence, preadsorption

of an intermediate ordered OTS submonolayer is a recommended procedure to prepare ordered, amino-functionalized silane films of monolayer thickness.

Two coupling experiments with pentafluorobenzaldehyde as a first test for the binding capacity of a mixed OTS:AHTMS sample gave yields of 18% and 34%, which compares to 21–44% for the coupling reaction with neat AHTMS films.

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