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A Near Edge X-ray Absorption Fine Structure Spectroscopy and X-ray Photoelectron Spectroscopy Study of the Film Properties of Self-Assembled Monolayers of Organosilanes on Oxidized Si(100)

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n-Alkyltrichlorosilane films with different alkyl chain length (*n*-propyltrichlorosilane [PTS, $CH_3(CH_2)_2SiCl_3$]; *n*-octadecyltrichlorosilane [OTS, $CH_3(CH_2)_{17}SiCl_3$]; *n*-triacontyltrichlorosilane [TCTS, $CH_3(CH_2)_{29}SiCl_3$]) and trimethoxysilane films with amino- and methyl-terminated alkyl chains (*n*-octadecyltrimethoxysilane [OTMS, $CH_3(CH_2)_{17}Si(OCH_3)_3$]; (3-aminopropyl)trimethoxysilane [APTMS, $NH_2(CH_2)_3Si(OCH_3)_3$]; (17-aminoheptadecyl)trimethoxysilane [AHTMS, $NH_2(CH_2)_{17}Si(OCH_3)_3$]) of different chain length have been characterized using near edge X-ray absorption fine structure (NEXAFS) spectroscopy and X-ray photoelectron spectroscopy (XPS) to probe the molecular order and orientation in self-assembled films. Furthermore, the influence of the different headgroups (trichlorosilanes vs trimethoxysilanes), chain lengths, and chain terminal functions (methyl vs amino) on the resulting film structures was investigated. It was found that methyl-terminated silanes with an alkyl chain of intermediate length like OTS and OTMS tend to form self-assembled monolayers which are oriented almost perpendicular to the surface. The different chemistries of these two compounds during adsorption seems to result in slightly different film structures. Aminosilane (AHTMS) films of the same chain length as OTS and OTMS, however, are completely disordered. XPS indicates, that this is probably due to the interaction of the amino group with the surface. Short alkyl chain silanes with a terminating methyl or amino group (APTMS, PTS) result in films with no defined orientation of the molecules. Also long chain methyl-terminated alkylsilane films (TCTS) are less well oriented than OTS films, which gives evidence that there is an optimal chain length for ordering in self-assembled organosilane films.

1. Introduction

It is well known that *n*-alkyltrichlorosilanes[1] and *n*-alkanethiols[2] form monolayers on either metal or oxidized surfaces through self-assembly from dilute organic solutions. Especially organosilanes have been used for many years to improve adhesion of polymers to oxidized substrates.[3−5] They also have applications in biosensors for protein immobilization,[6] as lubricants,[7] and as bonded phases in liquid and gas chromatography[8] and are considered for possible applications in molecular electronics.[9] Functionalized compounds (e.g. amino-, vinyl-, mercaptosilanes, etc.) offer pathways to self-assembled multilayer structures with properties of commercial interest.

The properties of these films, i.e. the chemical composition, thickness, orientation, and the lateral order of the alkyl chains, have been investigated extensively in the last few years. Wasserman et al.[10] have applied ellipsometry, contact angle measurements, and XPS to study wettability, thickness, and chemical composition. Tillman et al.[11] and Pomerantz et al.[12] have studied the molecular orientation of alkyl chains in OTS monolayers on oxidized silicon by the use of Fourier transform infrared spectroscopy (FTIR) and determined a tilt angle of the alkyl chains ≤15° with respect to the surface normal. Cohen et al. investigated the growth behavior of OTS monolayers on oxidized silicon with FTIR spectroscopy.[13] These measurements indicate film formation via partially ordered islands rather than via growth of a sparse homogenous layer. In contrast to this findings Wasserman et al.[14] and Tidswell et al.[15] suggest a "uniform" growth mode of the

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OTS monolayers on the basis of X-ray grazing incidence diffraction and X-ray reflectivity measurements. Water contact angle measurements of several groups[10,16,17] on *n*-alkyltrichlorosilane films of different chain length gave values of 111−115° for long chain silanes indicating the presence of densely packed methyl-terminated surfaces. For short chain compounds, lower values of ≤102° are reported, which imply a more loosely packed structure of methylene-terminated surfaces, indicating substantially disordered films.

Recently near edge X-ray absorption fine structure (NEXAFS) spectroscopy has been developed into a powerful technique to determine the orientation of molecules adsorbed on surfaces.[18] Fast data acquisition and analysis and high sensitivity offer a variety of advantages compared to infrared reflection−absorption spectroscopy. In combination with X-ray photoelectron spectroscopy (XPS) a complete analysis of thin organic films concerning molecular orientation, film composition, thickness, and chemical modification is possible.

In this paper we report recent results from NEXAFS and XPS measurements of *n*-alkyltrichlorosilane films with different alkyl chain length and amino-group and methyl-group terminated short and long chain trimethoxysilane films. Amino-terminated alkyltrichlorosilanes are not accessible as the amino group would readily substitute the chlorine atoms, whereas amino-terminated alkyltrimethoxysilanes are stable.

Our results provide evidence for an alkyl chain length dependent molecular orientation in methyl-group terminated organosilane films. Short alkyl chain silane adsorption results in disordered multilayer-type films. Long alkyl chain silanes form well-ordered monolayers. Amino-terminated long alkyl chain silanes, however, are disordered due to chemical interactions of the amino groups with the substrate.

2. Experimental Section

Film Preparation. All silane films were prepared under cleanroom conditions (class 100). The substrates were cut from Si(100) wafers. Prior to film preparation the substrates were cleaned by a wet chemical treatment in a freshly prepared hot acid mixture (H_2SO_4/30% H_2O_2 (3:1)) for 1 h followed by an extensive rinse with ultraclean water (Millipore) and a nitrogen dry blow.[20,16] Film preparation was performed by immersing the Si substrates into a dilute solution of *n*-propyltrichlorosilane PTS (ABCR), *n*-octadecyltrichlorosilane OTS (Merck), or triacontyltrichlorosilane TCTS (ABCR) in bicyclohexyl (Fluka) or into a solution of *n*-octadecyltrimethoxysilane OTMS (Fluka), (17-aminoheptadecyl)trimethoxysilane AHTMS in bicyclohexyl, or (3-aminopropyl)trimethoxysilane APTMS (Sigma) in ethanol for various periods of time. To remove excess silane aggregates resulting from polymerization in solution, the samples were rinsed with Millipore water and stirred in a chloroform bath for several minutes. Then they were blown dry with nitrogen. If there was still some excess polymer visible under a fiber optical illuminator, the samples were wiped with a soft 100% cotton cloth which was dipped in chloroform. As the short chain silane PTS tends to polymerize already in solution, the solutions were filtered before immersing the substrates (0.5 and 0.2 μm).

XPS. The XPS experiments were carried out on a Leybold MAX-200 spectrometer using Mg Kα and Al Kα sources. The X-ray source was operated between 200 and 300 W dissipated power. Survey spectra were recorded prior and after the XPS experiments in order to check for beam damage of the films. No changes could be detected in the survey spectra for the experimental conditions applied.

The experimental resolution was measured to be 0.9 eV. Electron binding energies were calibrated against the C 1s emission at E_b = 284.6 eV. The base pressure in the chamber was better than 10^{-9} mbar. Collected data were analyzed with a least-squares fit routine. Quantitative analysis was performed using a Shirley background subtraction routine.

The attenuation of the Si 2p peak of the substrate silicon (the low binding energy component from Si^0) was used to determine the thickness of the adsorbed layers. A mean free path of 35 Å according to Hensen et al.[21] for a photoelectron energy of 1200 eV was used and scaled with $E/(\ln E - 2.3)^{22}$ yielding 39 Å for the mean free path of Si 2p photoelectrons for excitation with Al Kα radiation (E_{kin} = 1388 eV) and 34 Å with Mg Kα radiation (E_{kin} = 1155 eV), respectively. For the average thickness determinations, an experimental error of 10 to 15% is estimated, mainly caused by the uncertainty in the escape depths.

NEXAFS. The NEXAFS spectra were recorded at the synchrotron radiation facility BESSY in Berlin at the monochromator HE-TGM 2. The energy resolution was better than 0.8 eV at the C 1s edge. To determine the orientation of the molecules, the angle of incidence of the photons was varied between 90° (normal incidence) and 20° (grazing incidence). Typically, spectra were recorded for two (20°, 90°) or three different angles of incidence (20°, 50 or 55°, 90°), only in some special cases were spectra also recorded at additional angles. Calibration of the energy scale was performed by recording to Au 4d absorption edge in first and second order. All spectra were taken in the partial yield mode using a retarding voltage of −150 V at the carbon K-edge. The base pressure in the chamber was better than 2 × 10^{-9} mbar. All spectra were taken at room temperature. The energy region for the C 1s edge was chosen between 280 and 320 eV.

NEXAFS data of molecules containing hydrocarbon chains are dominated by the C 1s absorption edge and several resonances, mainly a C−H* resonance at 287 eV and a C−C σ^*-resonance at 293 eV.[23] As the electronic transitions from the C 1s orbital into the unoccupied molecular orbitals obeys the dipole selection rules, the resonances show a strong angular dependence on the incidence angle θ of the linearly polarized X-ray photons, i.e. a polarization dependence.

From the variation of these two resonances with θ the orientation of the molecules can be determined, if the directions of the transition dipole moments (TDM), governing these transitions are known.[24]

The procedure employed for the determination of tilt angles from difference spectra is described in detailed in a recent NEXAFS study on the orientation of fatty acid Langmuir−Blodgett films on oxidized silicon substrates.[25] The difference spectra are calculated by subtracting the spectrum at a reference angle of incidence θ_d from the spectrum at a given angle of incidence θ. Thus, the angle-dependent features are isolated from the isotropic features of the spectra (mainly the absorption edge). The difference intensity of the resonances is then determined by numerical integration, for the CH resonance between 286 and 290 eV and for the CC resonance between 292 and 297.5 eV. From these intensities, the desired polar tilt angle of the alkyl chains α can be calculated using the equation[23,24]

$$I_{CH}(\theta) - I_{CH}(\theta_d) = PS_{\psi}\left(\frac{3}{2}\sin^2\alpha - 1\right)(\cos^2\theta - \cos^2\theta_d)$$

where P is the degree of polarization of the incident photons and S_{ψ} contains the excitation probability for the given resonance. S_{ψ} can be determined using a reference system containing alkyl chains with known molecular orientation, i.e., a Langmuir−

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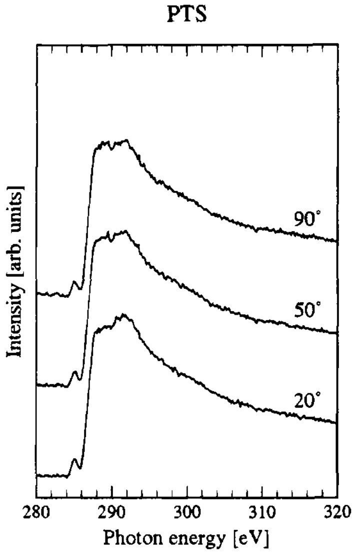

Figure 1. Series of NEXAFS spectra for PTS for different angles of incidence θ ranging from 20° to 90°.

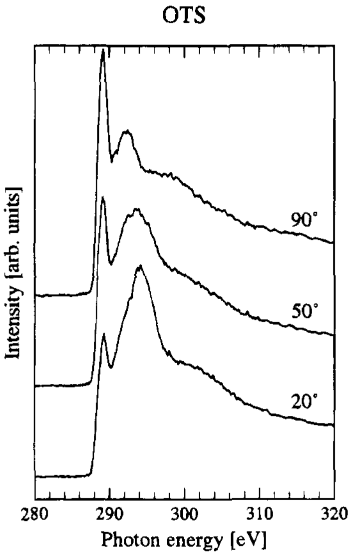

Figure 2. Series of NEXAFS spectra for OTS for different angles of incidence θ ranging from 20° to 90°.

Blodgett multilayer of calcium arachidate with perpendicular orientation of the alkyl chains.[25] A similar expression describes the angular variation of the CC resonance.

The above equation is valid for the CH resonance assuming TDMs oriented perpendicular to the alkyl chains and a random azimuthal orientation of the alkyl chains. The polarization dependence is proportional to $^3/_2 \sin^2 \alpha - 1$, i.e. maximal for $\alpha = 0°$ and zero for $\alpha = 54.7°$ (magic angle).[18] On the other hand, the polarization dependence should vanish for a random orientation of the TDMs. Note, that with NEXAFS only *average* molecular tilt angles can be determined.

3. Results and Discussion

3.1. *n*-Alkyltrichlorosilane Films. Methyl-terminated alkyltrichlorosilanes with three different chains lengths were investigated, namely PTS, OTS, and TCTS. Immersion time was 24 h in 100 mM solution for OTS and TCTS, while the PTS sample was immersed for 3 h in a 1 mM solution (see below).

Survey and single scan XPS spectra of these films were taken. In all cases, the survey spectra show only three elements: silicon (Si 2s, 2p), carbon (C 1s), and oxygen (O 1s, 2s, Auger KLL). Single scan spectra do not exhibit any feature characteristic for chlorine still present in the film, which indicates that complete reaction of the *n*-alkyltrichlorosilane molecules with the surface hydroxyl groups or traces of water had occurred. The XPS results agree very well with earlier measurements reported by Wasserman et al.[10]

For PTS an average film thickness of 13 Å was found, which is significantly higher than the theoretical length of the molecules (7.3 Å). XPS analyses of OTS and TCTS layers yielded film thicknesses of 27 and 43 Å, respectively, which are in good agreement with the theoretical values of 26.8 and 42.5 Å.

This indicates that OTS and TCTS had actually formed monolayers, whereas PTS seems to form multilayers even for the shorter immersion time in dilute solution. These XPS results are supported by earlier results from atomic force microscopy (AFM), ellipsometry and contact angle measurements.[16] Therefore, we have not investigated PTS with longer immersion times and/or higher concentrations. However, as the experimental error for the thickness determination for the short chain silanes is rather high due to uncertainties in the electron escape depth, we cannot rule out that also PTS forms a monolayer as would be expected.

Figure 1 shows a series of NEXAFS spectra of the PTS film. No strong changes can be seen in the spectra when going from normal incidence (90°) to grazing incidence (20°). The corresponding difference spectra (normal − grazing incidence, not shown) show virtually no signal at all. Only a slight change in the C−C σ^*-resonance can be observed (strongest intensity for grazing incidence) while the C−H* resonance remains almost constant. This lack of angular dependence for the resonances could be due to a tilt angle close to 55° (magic angle) or to a random orientation of the molecular axes in the films and/or a high concentration of gauche conformations in the chains. On the basis of the contact angle measurements[10,16] a uniform tilt angle of 55° can be ruled out. Instead it is concluded that the molecules show no preferred orientation and that the alkyl chains contain a high density of gauche conformations.

Figure 2 shows the NEXAFS spectra of OTS (from the same sample on which the XPS analysis was done). The intensities of the different resonances vary strongly when the angle of the incident photons is changed. The C−H* resonance is strongest for normal incidence while the C−C σ^* resonance is strongest for grazing incidence. From this it can already be concluded that the chains are oriented mainly normal to the surface. For a more elaborate quantitative analysis difference spectra of the various incidence angles and 50° were calculated. The difference intensities of the different resonances were then used to determine the tile angle of the alkyl chains as described above. This procedure yields a tilt angle α of less than 10°.

Figure 3 shows a series of spectra at the C 1s edge of a monolayer of TCTS (according to the XPS analysis). For this long chain silane the angular variation in the spectra is somewhat weaker than for OTS. A quantitative analysis yields an average tilt angle of 15 ± 10°. Note, however, that there is some indication for a thin disordered layer at the film−air interface in the case of the TCTS which will be discussed below.

A second issue besides the chain length dependence of monolayer formation was the investigation of the growth behavior of these films. In order to get information about the molecular orientation in incomplete OTS films in the island stages, NEXAFS measurements of silicon samples which were immersed for 15 s, 1 min, and 5 min in 1 mM OTS solutions were recorded. AFM measurements have shown that immersion in 1 mM solutions leads to the growth of branched islands[16] similar to that observed for OTS on mica.[19] Figures 4, 5, and 6 show the series of spectra at the C 1s edge of the three samples. They clearly

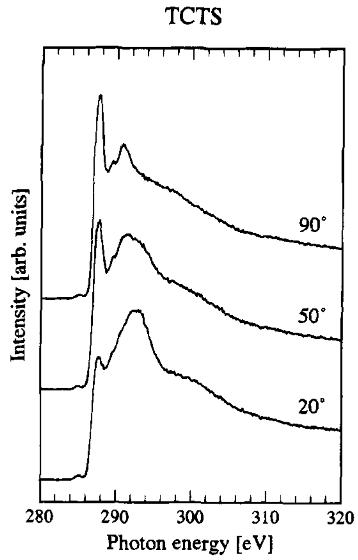

Figure 3. Series of NEXAFS spectra for TCTS for different angles of incidence θ ranging from 20° to 90°.

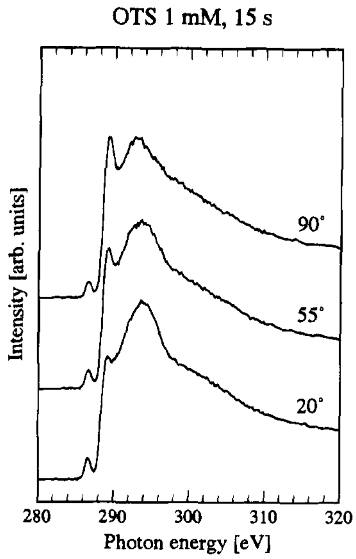

Figure 4. Series of NEXAFS spectra for a silicon sample, which was immersed for 15 s in a 1 mM OTS solution, for different angles of incidence θ ranging from 20° to 90°.

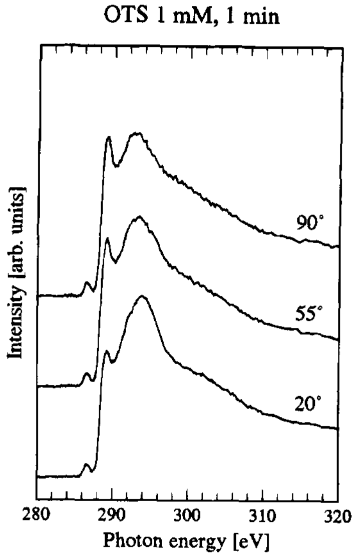

Figure 5. Series of NEXAFS spectra for a silicon sample, which was immersed for 1 min in a 1 mM OTS solution, for different angles of incidence θ ranging from 20° to 90°.

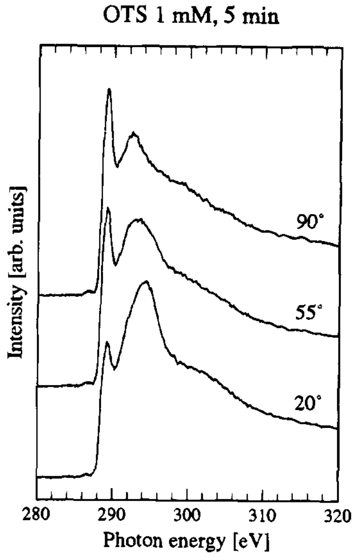

Figure 6. Series of NEXAFS spectra for a silicon sample, which was immersed for 5 min in a 1 mM OTS solution, for different angles of incidence θ ranging from 20° to 90°.

demonstrate that the intensities of the different resonances vary with the incidence angle of the photons. The quantitiative analysis yields average tilt angles of 40° ± 5° for the 15-s and the 1-min sample and 28° ± 5° for the 5-min sample. Obviously, even in the island stages of the film, there seems to be some preferential orientation of the molecules. These findings are in contrast to earlier reported NEXAFS results by Hähner et al.[26] of long alkyl chain alkanethiols, which show no preferred orientation in the early film stages. The small features in the spectra at 287 eV are indicative of C=C double bonds and have to be attributed to substrate contaminations.

The NEXAFS data together clearly demonstrate that there is a significant difference in the orientation inherent in organosilane films depending on the chain length. From XPS it can be concluded for all molecules that a successful and complete reaction occurs, since chlorine could not be detected in any case. The layer thicknesses which were determined by the attenuation of the substrate XPS peak agree with the thicknesses of a monolayer for OTS and TCTS. For the short silane PTS however, the determined thickness is approximately 2 times the value one would expect for a monolayer. This may indicate formation of multilayers but, as discussed above, the experimental error is rather high for these measurements. The PTS film does not exhibit a preferential orientation of the alkyl chains. Obviously, the chains are too short and the van der Waals interactions too small to force the chains into an ordered array.

For OTS, where the chain length is increased to 18 C atoms, the self-assembly process results in well-ordered and oriented films. A similar enhancement of molecular alignment has been oserved in the case of alkanethiols on gold,[27] where a high degree of molecular orientation is only observed for chains with more than about 16 C atoms.[28] Only for long chains is the van der Waals interaction between the molecules strong enough to enforce trans conformation and an alignment of the alkyl chains as in the bulk structure of hydrocarbons. It is interesting to note that in self-assembled films of alkanethiols on

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gold the hydrocarbon chains are significantly stronger tilted (between 30°[27] and 35°[26,28]) than in the case of OTS in Si substrates. As the tilt angle is related to the density of alkyl chains, this fact indicates that the density of hydroxyl groups, which anchor the silanes to the substrate, is higher than the density of S atoms (1 per 21.6 Å^2) in the ordered $(\sqrt{3} \times \sqrt{3})R\,30°$ structure of alkanethiols on Au(111).[27] Indeed a hydroxyl group density of 1 per 20 Å^2 on native silicon oxide has been reported by Wasserman et al.[14]

NEXAFS spectra of incomplete OTS monolayers demonstrate partial order as it would be expected for an island type growth mode and could be confirmed by recent AFM studies.[16] The average tilt angles of 40° for 15-s and 1-min immersion into the OTS solution and 28° for 5-min immersion are very likely caused by a higher degree of gauche conformations in the alkyl chains of the OTS molecules aggregated in the islands or an increasing tilt angle around the perimeter of the islands ("mushroom effect"). The decrease of the tilt angle down to 0° in the "final" OTS films can be explained by assuming a slow ordering process where the chains undergo a transition to an all-trans conformation thus maximizing their van der Waals interaction and minimizing their surface energy in the last step of the growth process.

For the longest chain (TCTS) the value of 15° for the average tilt angle had probably to be interpreted as stemming from molecules with their axis oriented mainly normal to the surface with additional adsorbed molecules on top of the monolayer. This interpretation is based on the observation that the CH resonance intensity plot from the NEXAFS data (cf. Figure 7a) does not vary linearly with $\cos^2 \Theta$ as in the other samples. The same is true for the CC resonance (Figure 7b).

Such a behavior can be explained assuming a two-layer model for the TCTS film with a thin disordered (or strongly tilted) top layer and a highly oriented (perpendicular) "bulk". Depending on the geometry of the experiment and the thickness of the top layer, the signal from the latter will dominate the spectra at glancing incidence while for normal incidence the attenuation of the "bulk" signal is weak, resulting in the curved shape of the plot in Figure 7 (solid line).

We could obtain reasonable agreement of the model with the data only by assuming a top layer thickness of significantly less than the escape depth of the electrons of 15 Å,[18] namely 10 Å. It has to be noted, that we have to assume different average tilt angles for the top layer in order to explain the behavior for the two resonances (46° for the CH resonance and 55° for the CC resonance, respectively). For earlier work[26] it is known that this observation is indicative of high conformational disorder, i.e. a substantial degree of gauche conformations in the alkyl chains in the top layer.

Compared to the "bulk" of the film, the film/air interface shows some tilting or disordering in the case of TCTS. As the contact angle measurements indicate a mainly methyl-terminated surface ($\theta_{H_2O} = 113°$), tilting is more likely to be the reason for the observed behavior. Although this model provides good agreement with the experimental data, a higher tilt angle would imply a lower density of hydrocarbon chains in the film surface. This, however, is at odds with the assumption implicit in our model to explain the NEXAFS angular dependence (Figure 7) that deeper in the layer the chain density is (with a tilt angle close to 0°) already maximal. At present we believe that the presence of other inhomogenities (domain boundaries, defects) allows additional (nonordered) adsorption and causes this apparent inconsistency.

In our AFM study[16] we find an alkyl chain length dependent reactivity of the silanes, i.e. the monolayer of OTS is formed about 5 times faster than that of TCTS. This difference in reactivity may indicate differences in the adsorption mechanism as discussed below for the trichlorosilanes vs the trimethoxysilanes.

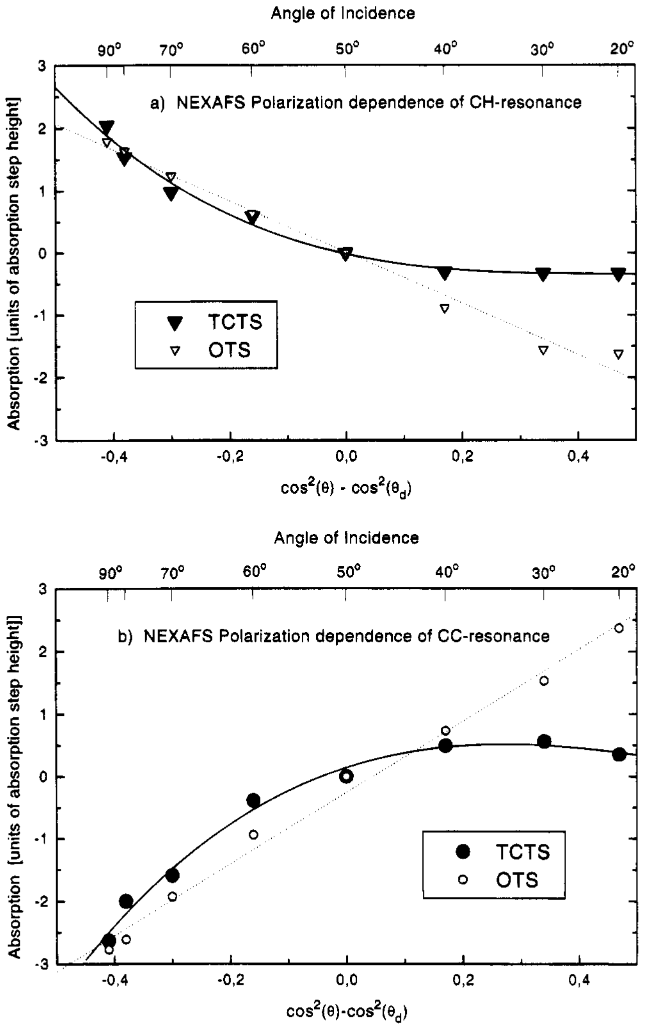

Figure 7. Difference intensities for TCTS and OTS vs $\cos^2(\theta) - \cos^2(\theta_d)$ ($\theta_d = 50°$): a (top), CH resonance; b (bottom), CC resonance.

The short chain silane (PTS), however, does not form an ordered film which is probably due to the weak van der Waals interactions which are not sufficient to induce chain ordering.

3.2. Trimethoxysilane Films. Silicon samples were immersed for 24 h in 100 mM solutions of (3-aminopropyl)-trimethoxysilane (APTMS) in ethanol and (17-aminoheptadecyl)trimethoxysilane (AHTMS) and *n*-octadecyltrimethoxysilane (OTMS) in bicyclohexyl, respectively.

XPS survey and single scan spectra of APTMS show contributions from the substrate and the film: silicon (Si 2s, 2p), carbon (C 1s), oxygen (O 1s, 2s, Auger KLL), and nitrogen (N 1s). The detection of nitrogen indicates successful film deposition, since this element is only contained in the film material. Figure 8 shows the N 1s peak deconvoluted into two different nitrogen species occurring in different binding states. One species can be located at 399.3 eV and one at 401.1 eV binding energy, which are characteristic for aliphatic amino groups and protonated aliphatic amino groups. From the attenuation of the Si 2p peak, a layer thickness 10 Å was calculated (theoretical value for a monolayer is 8.5 Å).

NEXAFS spectra of the APTMS film are shown in Figure 9. As for the short chain PTS the resonances do not vary with the angle of the incident photons. This resembles the situation with PTS described above and indicates the

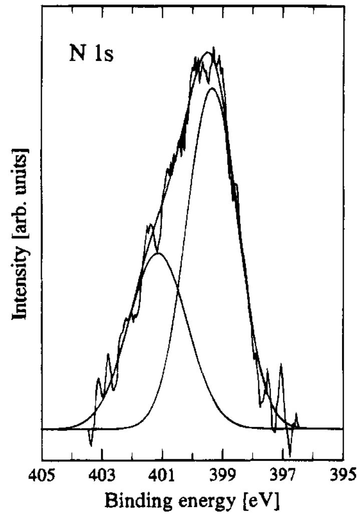

Figure 8. Single scan XPS spectrum of the N 1s region of an APTMS film on a silicon substrate. It can be distinguished between at least two different nitrogen species, which are characteristic for free aliphatic and protonated species.

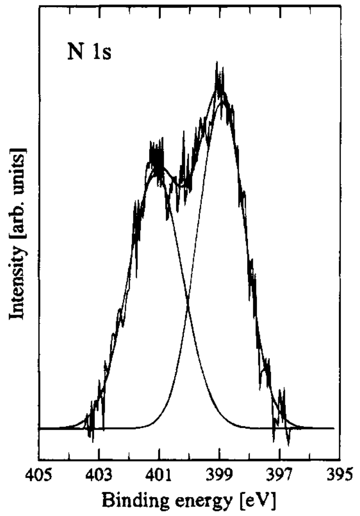

Figure 10. Single scan XPS spectrum of the N 1s region of an AHTMS film on a silicon substrate. It can be distinguished between at least two different nitrogen species, which are characteristic for free aliphatic and protonated species.

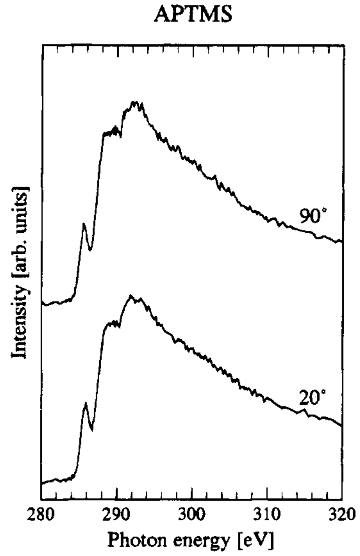

Figure 9. Series of NEXAFS spectra for APTMS for 20° and 90° angles of incidence.

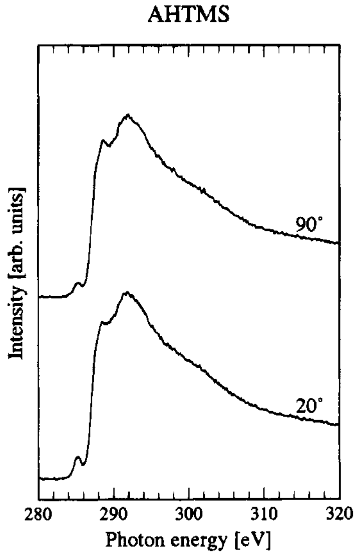

Figure 11. Series of NEXAFS spectra for AHTMS for 20° and 90° angles of incidence.

presence of a disordered film possibly consisting of more than one monolayer.

AHTMS film deposition could be confirmed by XPS. As with APTMS, the nitrogen signal indicated film deposition. Again, there are at least two different chemical binding states occurring which is shown in Figure 10. The binding energies agree with values for free aliphatic amino groups and their protonated derivates. Film thickness was determined and found to be 39 Å, which is significantly higher than the theoretical value of 26.7 Å. This is indicative for establishing an incomplete second layer on top of the first supported by a higher amount of protonated amino groups (Figure 10). Figure 11 displays the NEXAFS spectra of the long alkyl chain aminosilane at the C 1s edge. The spectra do not vary with photon incidence angle. Therefore the AHTMS film must be disordered. This is in striking contrast to the behavior of the methyl-terminated trichlorosilane with the same chain length (OTS); see previous section.

In order to get information about the reason of this unexpected behavior of AHTMS layers, NEXAFS spectra of OTMS were taken in order to decide whether the chain-terminating amino group or the different bonding reactivity of the silanes (i.e. trichloro vs trimethoxy) are leading to this observation (Figure 12). The different resonances in the OTMS spectra vary strongly with the incident angle of incoming photons. A quantitative analysis yields an average tilt angle of 20° ± 5°. This indicates that the presence of the terminating amino group is the main reason for the disordering when going from OTS to AHTMS.

The exchange of the terminating methyl groups against amino groups in long chain alkylsilane films thus leads to significant disorder in the deposited monolayers. Since XPS spectra show at least two different binding states for nitrogen which can be assigned to aliphatic neutral and aliphatic protonated amino groups, disorder may be caused by acid–base interactions of the AHTMS molecules with either surface silanol groups or silanol groups of the silane molecules after partial hydrolysis. A second possible explanation could be repulsive dipole–dipole interactions between the amino groups, since amino functionalities exhibit non-negligible dipole moments of > 1 D as inferred from the value for ethylamine (1.22 D).[29] Note, that interaction of the amino groups with atmospheric carbon dioxide leading to carbamate formation could also inhibit

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(29) *CRC Handbook of Chemistry and Physics*, 70th ed.; Weast, R. C., Lide, D. R., Astle, M. J., Beyer, W. H., Eds.; CRC Press, Inc.: Boca Raton, FL, 1989.

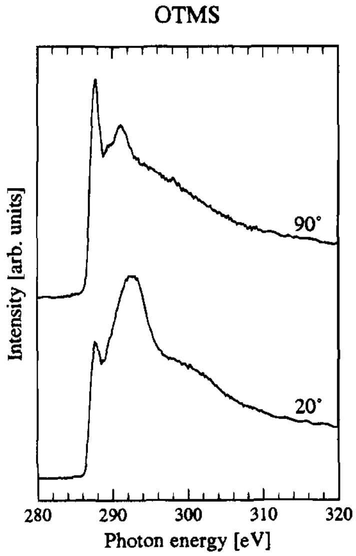

Figure 12. Series of NEXAFS spectra for OTMS for 20° and 90° angles of incidence.

order formation. IR measurements in our group, however, give no evidence for carbamate formation.[30]

NEXAFS spectra for the short chain aminosilane APTMS and the long chain aminosilane AHTMS do not exhibit angular variations of the resonance intensities at the C 1s edge. In contrast to the *n*-alkyltrichlorosilanes all amino-terminated films show a significant degree of disorder.

The influence of the trimethoxysilyl group compared to the trichlorosilyl group is indicated by the higher tilt angle of OTMS (20° ± 5°) as compared to OTS (0° ± 5°). The long chain methyl-terminated trimethoxysilanes as well as the trichlorosilanes form well ordered layers. The higher average tilt angle of OTMS as compared to OTS could be due to a different adsorption mechanism of the trimethoxysilane molecules, since methoxy groups are less reactive than chlorine atoms.

A possible scenario for the formation of the films is as follows: OTS reacts rapidly with traces of water to form OTS oligomers in solution. In these oligomers, the alkyl chains are already closely packed in order to minimize their energy via van der Waals interactions. However, complete polymerization in two dimensions is not possible due to the space constraints imposed by the chains. Thus there will be residual silanol (Si–OH) groups dangling from the two-dimensional network.

When the oligomers diffuse to the substrate surface, they may physisorb to the surface prior to chemisorption. If the mobility is high enough, formation of the large islands mentioned above (0.9 μm) and described in ref 16 can be understood through clustering of oligomers. The driving force for this step is the lateral interaction between oligomers (two-dimensional condensation). This mechanism would also account for the branched (fractal) shape of the islands.

The last and slowest step in monolayer formation, supposedly, is the chemisorption to the surface, i.e. elimination of water and formation of Si–O–Si bonds to the substrate.

The apparent decrease of the tilt angle of the monolayers close to their completion, which was only observed for the OTS samples, can then be explained by a slow ordering process caused by the adsorption of OTS monomers into the nearly complete film which fill up vacancies and voids and leads to a density of alkyl chains sufficient to force the molecules into a perpendicular all-trans configuration. The large time constant of this process is comparable to observations on self-assembled long chain alkanethiols on gold.[26]

The situation for the trimethoxysilanes and possibly the longer chain trichlorosilanes is different: these species are less reactive, which means that hydrolysis and oligomerization in solution are suppressed. Instead of oligomers, mainly monomers react with the surface. As the monomers on the surface are less mobile than they would be in solution, the two-dimensional polymerization is sterically hindered compared to the situation in the oligomers described above. Thus the packing of the alkyl chains will be less dense and consequently the tilt angle will be higher.

Even for long immersion times, the alkyl chain density will be lower than that for the OTS films, as the reactivity of the monomers is not sufficient to react with all available surface sites.

The reduced surface reactivity of the trimethoxysilanes is supported by recent XPS results[31] which show slower adsorption kinetics of trimethoxysilane films as compared to trichlorosilane films applying the same film preparation conditions (1 mM solution).

4. Conclusions

The ordering behavior of *n*-alkyltrichlorosilane films was found to be alkyl chain length dependent. An optimal chain length for ordering seems to be present in OTS films, since the alkyl chains are in all-trans conformation oriented perpendicular to the surface.

Long alkyl chain silanes like TCTS, however, form less well ordered films whereas short alkyl chain silanes (PTS) result in disordered films. The behavior of the TCTS films could be explained assuming a two-layer model with a disordered film/air interface and a highly oriented bulk.

Reactivity differences between trichlorosilanes and trimethoxysilanes result in slightly more disordered trimethoxysilane films, since the molecular density in the latter films is smaller due to incomplete lateral polymerization.

Unexpectedly aminosilane films with the same chain length as OTS are found to be disordered. This is presumably caused by acid–base interactions between amino and silanol groups as supported by XPS measurements which give evidence for free and protonated amino groups. In addition, repulsive dipole–dipole interactions could influence the growth and ordering behavior of the molecules, which are carrying non-negligible dipole moments.

This does not necessarily mean that these reagents are not suited as coupling agents, since protonation of the amino groups may be reversible, i.e. the coupling capacity need not necessarily be deteriorated due to this interaction.

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(30) Unpublished IR data, P. Harder.

(31) Unpublished XPS results, K. Bierbaum.