The Structure of n-alkyltrichlorosilane monolayers on Si(100)/SiO₂

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Abstract

The structure of n -alkyl-trichlorosilane self-assembled monolayers (SAMs) of alkyl chain lengths $n = 12, 14, 18, 22$ formed on the amorphous native oxide of silicon (100) has been investigated via Å-resolution surface x-ray scattering techniques, with particular focus on the proliferation of lateral order along the molecules' long axis. Grazing incidence diffraction shows that the monolayer is composed of hexagonally packed crystalline-like domains for $n = 14, 18, 22$ with a lateral size of about 60 Å. However Bragg Rod analysis shows that ~ 12 of the CH₂ units are not included in the crystalline-like domains. We assign this, and the limited lateral crystallites' size, to strain induced by the size mismatch between the optimal chain-chain and headgroup-headgroup spacings. Analysis of X-ray reflectivity profiles for $n = 12, 14$, and 22 show that the density profile used to successfully model $n = 18$ provides an excellent fit where the analysis-derived parameters provide complementary structural information to the grazing incidence results.

Introduction

Self-assembled monolayers (SAMs) have been intensely studied since their inception in the 1980s.¹⁻⁵ Their many applications range from liquid crystal alignment⁶, organic field-effect transistors⁷, photovoltaic devices⁸, biosensors⁹ and enzyme electrodes¹⁰ to adhesion promoters¹¹ and lubricants.¹² For basic science, they are intriguing model systems for the study of self-organization in two-dimensional matter under the complex interplay of van der Waals (vdW), covalent and electrostatic interactions.³ The most widely studied and utilized SAMs are *n*-alkyl-trichlorosilanes ($\text{CH}_3(\text{CH}_2)_{n-1}\text{Cl}_3\text{Si}$, denoted *Cn*-TS) on the native oxide which forms on silicon wafers (Si/SiO_2), where C18-TS (octadecyltrichlorosilane, which is often abbreviated as OTS or OTDS in the literature) is the most commonly used molecule.^{3-5,13,14} Previous studies of C18-TS SAMs have shown that the molecules are standing up and hexagonally packed laterally.^{4,15} The monolayer’s exceptional stability is attributed to a combination strong molecular surface bonding and extended lateral siloxane cross-linking ($-\text{Si}-\text{O}-\text{Si}-\text{O}-$).^{3,5} However, the exact bonding scheme and the structure determining factors within the monolayer are not fully resolved.^{3,14,16-21} In particular, it is still unclear how the size-mismatch between chain-chain separation and Si-O-Si dominated head group spacings influences the SAM’s structural properties.^{3,22} In order to gain a deeper insight, we have varied the number of CH_2 units in the chain so as to modify the relative strength of the interchain interaction, which increases linearly with *n*.²³ In this paper, we have used *n* = 12, 14, 18, and 22. Tidswell et al.’s pioneering X-ray reflectivity (XRR) (*Cn*-TS²⁴) and grazing incidence diffraction (GID) (C18-TS¹⁵) investigations of SAM systems served as a starting point for the present study. In the following, we present a significantly higher resolution x-ray study of these SAMs, based on larger- q_z -range XRR measurements, a more physical electron density model, and detailed GID and Bragg Rod (BR) measurements, modeling and interpretation. The combined XRR, GID and BR study of four different chain lengths provides the most comprehensive structural investigation of *Cn*-TS SAMs to date.

Experimental section

Cn-TS monolayers were prepared on Si(100)/SiO₂ at room temperature and at relative humidities of $\sim 30\%$ by standard solution-based procedures using bicyclohexyl as the anhydrous solvent, providing an optimal environment for the formation of smooth monolayers^{14,25,26} (for details see our recent studies^{27,28}). Molecules were obtained from Gelest ($n = 12, 14, 22$) and Sigma Aldrich ($n = 18$). We have used alkyl-silanes as received in fresh bottles, in order to reduce the deleterious effects of water induced bulk cross-polymerization which occurs when exposed to humid air.²⁹ Note that C22-TS is only available as molecules in a blend, containing a non-negligible amount of shorter chain lengths, giving rise to slightly shorter effective average lengths. The surface-normal and lateral structure is probed utilizing synchrotron XRR and GID.

XRR measurements were performed at X22A, NSLS (C12-TS, C14-TS, C22-TS) and ID10, ESRF (C18-TS), with wavelengths $\lambda = 1.156 \text{ \AA}$ and $\lambda = 0.590 \text{ \AA}$, respectively. GID experiments were made at X22B, NSLS, with $\lambda = 1.517 \text{ \AA}$. To minimize radiation damage and air scattering, all measurements were carried out under a Helium atmosphere.

XRR measures $R(q_z)$, the interface-reflected intensity fraction of an x-ray beam incident on an interface at a grazing angle α . $q_z = (4\pi/\lambda) \sin \alpha$ is the surface-normal wave vector transfer.^{30,31} XRR is related, within the first Born-approximation, to the Fourier transform of the derivative of the surface-normal (z) electron density profile ($\rho(z)$) via the Master-formula^{30,31} $R(q_z) = R_F(q_z) \left| \rho_0^{-1} \int (d\rho(z)/dz) \exp(iq_z z) dz \right|^2$. $R_F(q_z)$ is the Fresnel reflectivity of an ideally smooth and abrupt interface. Detailed structural information can be obtained by constructing a model electron density profile, usually made up of slabs of constant electron density, which is then used in the master formula above to reproduce the experimental data by varying the parameters defining the model. In our previous studies^{27,28} on related systems we have shown that for reproducing faithfully the measured XRR of C18-TS on Si/SiO₂ with physically meaningful parameter values, it is imperative to use a model with 5 sub-layers. These represent (1) a density dip at the Si/SiO₂ interface caused by the bond

density mismatch between Si and SiO₂, (2) the native silicon oxide layer, (3) a low density monolayer region near the substrate, (4) a high density region at the Si-O-Si cross-links, and (5) the hydrocarbon chains. We note that regions (3), (4) and (5) are consistent with the schematic illustration in Ref. 22. We use this detailed model in the present study.

GID and simultaneous BR measurements provide insight into the surface parallel order and crystallite size, as well as the surface normal crystallinity. Here, the X-rays' incidence angle α is kept smaller than the critical angle for total external reflection. In this case, an evanescent wave is formed, moving along the surface and penetrating only ~ 100 Å, probing, consequently, only the near-surface structure.^{32,33} The detector is scanned out of the reflection plane by an angle 2θ , yielding a lateral diffraction vector $q_r \approx (4\pi/\lambda) \sin \theta$, which probes the surface-parallel order. Soller slits provided a $\Delta q_r = 0.019$ Å⁻¹ (FWHM) with a Gaussian-like shape. Using a vertically-aligned position sensitive detector, we measure the surface-normal q_z -distribution of the intensity at each q_r position, thus providing a simultaneous BR measurement at GID peak positions. GID peaks can be described by a Lorentzian function, $I(q_r) = (I_0 \kappa_r / 2\pi) / [(q_r - q_0)^2 + (\kappa_r / 2)^2]$, which is convoluted with the experimental resolution function. From the fitted peak position, q_0 , and under the assumption of a hexagonal lattice, the in-plane lattice constant, a , is obtained via the relation $a = 4\pi / (\sqrt{3} q_0)$. The corresponding area per molecule is $A = a^2 \sqrt{3} / 2$. From the fit-obtained intrinsic peak width κ_r , the lateral crystalline coherence length is calculated via the Debye-Scherrer formula, $\xi \approx (0.9 \cdot 2\pi) / \kappa_r$.³⁴ This coherence length is associated with the domain size, where the correlation function has an effective exponential decay. The fall-off of the scattering intensity along q_z (the BR) results from the finite molecular length. In contrast to XRR, which also probes the scattered intensity's q_z distribution, the BR intensity is significant only at the GID peaks' positions. Thus, BRs provide information only on the ordered regions of the monolayer, while XRR averages over both in-plane and out-of-plane ordered and disordered regions. Quantitatively, this intensity distribution is the product of the z -dependent molecular form factor and the structure factor, multiplied by the surface enhancement factors,

$T(\alpha)$ and $T(\beta)$.^{32,33} The molecular form factor is the Fourier transform of the electron density distribution, and for cigar shaped molecules it can be approximated as a sinc-function along the long axis. The modulation period of the Bragg rod is inversely proportional to the length l of the part of the molecule included in the crystalline-like sub-layer. Accordingly, the scattering along q_z can be written as $I(q_z) \propto \left[(\text{sinc } Q_z l/2)^2 e^{-(Q_z \sigma_0)^2} \right] e^{-(q_z \sigma_z)^2} |T(\alpha)|^2 |T(\beta)|^2$ where $\text{sinc } Q_z l/2 = \frac{\sin Q_z l/2}{Q_z l/2}$.³³ Here, Q_z is the wave vector components along the molecules long axis which is related to q_z via the molecular tilt, t , and its azimuth, ϕ .³³ The factors $e^{-(Q_z \sigma_0)^2}$ and $e^{-(q_z \sigma_z)^2}$ represent the gradual decrease in electron density at the end of the molecule and the surface roughness, respectively. In the BR fits, the uncertainty of l , in our and in previous studies, is in the range of 10 – 15%, since l and σ are correlated.

Results and discussion

Fig. 1(a) shows the Fresnel-normalized measured reflectivities for $n = 12, 14, 18, 22$. All four curves show characteristic Kiessig fringes, which are typical of uniform monolayers having a different electron density than the substrate. These oscillations result from constructive and destructive interference of waves reflected from the monolayer's top and bottom interfaces and from the silicon/silicon-oxide interface as α is varied.^{30,31,35} The sharp and multiple minima clearly indicate that the films are of excellent quality since this condition only occurs for films which are spatially uniform. As expected, the modulation period increases with decreasing n . This corresponds to thinner layers for shorter chains. However, as we will show, the thinning is not proportional to n , as would be expected if for all n the monolayers were standing-up and closely packed. The electron density profiles obtained from the reflectivity analysis, solid lines in Fig. 1(a), are shown in Fig. 1(b). The five-slab density profile, developed in our recent XRR study of C18-TS on Si/SiO₂²⁸, also provides an excellent description for $n = 12, 14$, and 22. Further details on the fitting analysis are presented in the Supporting Information.

Figure 1: (a) Fresnel-normalized measured XRR (symbols) of C12-TS (◇), C14-TS (△), C18-TS (○) and C22-TS (□) on Si/SiO₂, and the corresponding model fits (lines). (b) The corresponding (same-color) fit-derived electron density profiles with (solid lines) and without (dashed lines) surface roughness. All curves are spaced vertically for clarity. (c) XRR fit-derived alkyl chain slab thickness (symbols) as a function of n , and the expected length of an extended molecule (dashed line). (d) XRR fit-derived electron density of the chain slab (black symbols) as a function of n , and the expected density for hydrocarbon chains packed in a rotator phase (dashed line).

The XRR fit-derived alkyl chain sub-layers thicknesses L are plotted versus n in Fig. 1(c) along with the predicted alkyl chain lengths (solid line), calculated from the projected C-C bond length of 1.27 Å/CH₂ (from the C-C bond length of 1.54 Å and bond angle of 113.8°³⁶). Whereas L is in good agreement with the calculation for C18-TS, for C12-TS, C14-TS, and C22-TS, L is slightly shorter than the calculation. Although the XRR results alone might suggest a molecular tilt, on the basis of the Bragg Rod analysis (see below) a tilt can be ruled out. For C22-TS we attribute the discrepancy, in part, to the contribution from the shorter length impurities (see experimental section). For C12-TS, and C14-TS the shorter length results from lower electron densities (discussed below).

The XRR fit-derived electron densities for the alkyl chain slab, ρ_{CH_2} , are plotted ver-

sus n in Fig. 1(d) along with the predicted electron density in the rotator phase, $0.31 - 0.32 \text{ e}/\text{\AA}^3$.^{33,37,38} For C18-TS, L and ρ_{CH_2} are in good agreement with the predictions, suggesting that the chains are all-trans, vertically aligned, and packed in a rotator-like phase. In previous measurements of C18-TS monolayers on Si/SiO₂, the alkyl slab density has ranged from $0.26 - 0.36 \text{ e}/\text{\AA}^3$.^{24,29,39-41} We note that the density should not exceed the value for alkane crystals in their fully crystalline orthorhombic phase $0.34 \text{ e}/\text{\AA}^3$.³⁸ Our results for C18-TS are in good agreement with long-chain alcohol monolayers on Si/SiO₂⁴² and sapphire⁴³ that form well-ordered SAMs with fully extended chains. In addition, the fit-obtained density of $0.25 \text{ e}/\text{\AA}^3$ for C12-TS agrees well with the densities ($0.25 \pm 0.01 \text{ e}/\text{\AA}^3$) obtained for long-chain alcohol monolayers on Si/SiO₂⁴² and sapphire⁴³ in the higher-temperature, stretched liquid phase. The fit-derived parameter values are provided in the Supporting Information. Of note is that of all four chain lengths studies, C18-TS exhibits the highest electron density, consistent with the largest crystalline coherence length shown by GID below.

Fig. 2(a-c) shows the GID diffraction maps in (q_z, q_r) -space for C_n -TS monolayers of $n = 14, 18$ and 22 . Note that no GID peak, and hence no BR, is observed for $n = 12$, even though a monomolecular layer is found by XRR above (a detailed discussion will follow below). For all other chain lengths, a single Bragg peak is found, in each case located at $q_r \approx 1.50 \text{ \AA}^{-1}$. This single peak is typical for monolayers made up of hydrocarbon chains that are hexagonally arranged in the rotator phase, be it Langmuir films^{37,44}, alkanes³³ or alcohols frozen at the free surface⁴⁵, or alcohol surface-frozen layers on Si/SiO₂⁴² and on sapphire.⁴³ The absence of higher order peaks originates from the very fast fall off of the form factor in the rotator phase.³³ However, unlike a true rotator phase, one end of each molecule has steric hindrance due to the chemical attachment with the surface and this prevents free rotation along the long molecule axis. The existence of a uniformly tilted phase can be ruled out since the BRs have their peaks at $q_z = 0 \text{ \AA}^{-1}$. The observation of the same BR type (albeit of different widths) for all chain lengths (except $n = 12$), suggests

Figure 2: (a,b,c) Measured GID intensity maps for C14-TS, C18-TS, C22-TS on Si/SiO₂ in (q_r , q_z)-space showing a BR, originating in the C n -TS monolayer; (d,e,f) measured GID peaks for C14-TS (Δ), C18-TS ($\circ$) and C22-TS ($\square$), and their resolution-function-convoluted Lorentzian fits (lines); (g,h,i) measured normalized BRs (symbols), and their corresponding model fits (lines). The blue lines are BRs calculated for the alkyl chain thickness lengths equal to the alkyl slab thicknesses obtained from XRR. The red lines corresponds to the best fit using the XRR determined Si/SiO₂ surface roughness of ≈ 3.5 Å.

the same basic molecular packing for $n = 14, 18$ and 22 . Since the underlying native oxide is amorphous, there is no preferred azimuthal orientation observed in the GID, consistent with the crystalline-like monolayer being a two dimensional powder. The GID data analysis, detailed below, agrees very well with GID studies of C18-TS on Si/SiO₂^{15,25,46} and our XRR findings.

In order to quantify these observations, the intensity distribution along q_r and q_z has been fit to simple models in order to obtain real space parameters. Fig. 2(d-f) shows the in-plane Bragg peaks for $n = 14, 18$ and 22 together with their fits, which reproduce the data excellently. The corresponding fit-derived parameter values and the resultant real space parameters are given in Table 1. In Fig. 3(a) the area per molecule derived from

Table 1: GID and BR fit-derived parameters for Cn -TS. The corresponding fits are shown in Fig. 2. (*) denotes values obtained with the roughness fixed at 3.5 Å.

	n	12	14	18	22
GID	q_0 (Å ⁻¹)	-	1.497±0.004	1.510±0.004	1.511±0.004
	A (Å ²)	-	20.34±0.06	19.99±0.06	19.95±0.06
	κ_r (Å ⁻¹)	-	0.112±0.001	0.085±0.001	0.100±0.001
	ξ (Å)	-	50±1	66±1	57±1
	l (Å)	-	2.0±1.3*	10.1±0.5*	11.7±0.5*

Figure 3: (a) GID fit-derived area per molecule as a function of n . (b) GID fit-derived crystalline coherence length as a function of n .

GID exhibits a decrease in the area per molecule with increasing n . Notice that the areas per molecule for C18-TS and C22-TS are in excellent agreement with those obtained for C18-TS on sapphire²⁷, suggesting that the interlayer packing is determined mainly by the vdW interaction between the alkyl chains, and rather independent of the nature of the substrate. In comparison, C14-TS has a slightly larger area per molecule, consistent with the XRR-derived electron density, which is smaller than the rotator phase value. For C12-TS the absence of a GID peak, in combination with the XRR-determined electron density of $\sim 0.25 e/\text{\AA}^3$ and a smaller than expected thickness, suggests that the molecules are arranged in the stretched liquid phase, which comprises on average surface normal aligned molecules, albeit not fully extended, that are laterally disordered, containing a significant fraction of

Gauche defects and twisted dihedral bonds.^{42,43} For C_n -TS monolayers the domain size is limited by the strain^{25,27} which originates in the competition between the lateral cross-linking Si-O-Si bond distance and the larger vdW diameter of a single hydrocarbon chain.³⁶ This is discussed in detail below in the context of the BR analysis. The fit-derived crystalline coherence length, ξ , as a function of n is shown in Fig. 3(b). Since ξ only corresponds to ~ 12 molecular diameters, we refer to the in-plane order as crystalline-like rather than crystalline. ξ has the highest value for C18-TS and is smaller for C14-TS and C22-TS, following the same n -dependence as ρ_{CH_2} .

To investigate the thermal evolution of the monolayers' structure, GID measurements of C18-TS have been carried out at temperatures between room temperature (RT) and 90°C. Fig. 4(a) shows the measured GID data along with its model fits. The fit-derived area per molecule increases linearly with temperature, see Fig. 4(b), where the areal expansion coefficient, $\alpha_A = (dA/dT)/A = 0.83 \cdot 10^{-3} \text{ K}^{-1}$. In contrast, the crystalline coherence length ξ is found to be temperature independent. Interestingly, the same α_A has been obtained for

Figure 4: (a) Measured GID peaks (symbols) and model fits (lines) for C18-TS ranging from RT to 90°C. (b) Fit-derived area per molecule (symbols) and linear fit as a function of temperature, yielding the areal thermal expansion coefficient discussed in the text.

C18-TS on sapphire²⁷ despite the presence of preferred orientational order. This suggests that the expansion is limited by the lateral cross-linking in combination with the vdW chain-chain interaction, rather than by the actual binding to the substrate. This is in contrast to surface-frozen alcohol monolayers on solid supports, where a dependence of the expansion

coefficient on the substrate is found.⁴² The absence of cross-linking in purely vdW-bound organic monolayers of alkanes and alcohols, supported either on their own melt or on liquid mercury^{47,48} results in a 40-100% larger α_A than that found here.

The measured BRs are shown in Figs. 2(g-i), along with the corresponding fits (red lines) and model curves (blue lines), calculated using the XRR-derived layer thickness L . Note

Figure 5: BR fit-derived surface normal crystalline-like sub-layer thickness l (red symbols) as a function of n , as discussed in the text. The dashed line shows the expected lengths of the fully extended chains, and the solid line is a linear fit to the red data points, using the same slope as the dashed line, as discussed in the text.

that there is only one reported BR measurement for Cn -TS on Si/SiO₂ that we are aware of and that is for C18-TS.²⁵ Whereas the data quality is sufficient to conclude that the molecules are untitled, the counting noise prevented a detailed BR analysis. For all chain lengths, we find that the BRs are more extended than the calculated model curve (blue lines). This implies that the crystalline-like layer is thinner than the fully extended chain: only part of the chains' length forms the crystalline-like layer. To quantify these findings, we fitted the BRs to the simple model described in Ref. 33. Here, the roughness σ_0 is set to the XRR-derived value of ~ 3.5 Å and the tilt angle t is set to 0° , as the BR maximum is at $q_z \approx 0$ Å⁻¹. The resulting thickness of the crystalline-like layer, l , is shown in Table 1, and displayed in the red symbols in Fig. 5. The possibility of the broadening of the BR stemming from a random distribution of small molecular tilt angles towards statistically distributed

azimuthal directions rather than from partial crystallinity, is considered and dismissed in the Supporting Information.

Fitting the l versus n data to a linear form yields the solid line shown in Fig. 5(a) with a slope of 1.26 ± 0.25 Å and an intercept of 12 ± 1 , suggesting that ~ 12 CH₂ groups in the alkyl chain don't contribute to the lateral order. For comparison, the theoretical lengths for extended chains are shown as the dashed line where the slope, 1.27 Å, is similar to that derived here from the red points, but the intercept is, of course, at $n=0$.

In the following, our GID and BR results for C_n -TS are compared and contrasted with previously published results of similar systems (see Table 2 for their real space parameters, ξ and l/L). These include Octadecyltrimethoxysilane (OTMS) which undergoes a similar, albeit slower, hydrolysis cross-linking reaction as to C18-TS.^{49–52} On the free water surface the OTMS monolayers's correlation length ξ varies between 35 – 80 Å⁵², similar to the correlation length reported here for C18-TS on Si/SiO₂. Significantly larger correlation lengths were found for Langmuir films of C_n OH on the free water surface^{53–55}, as well as surface-frozen alkanes supported by their own melt³³. For surface-frozen C18OH monolayers on amorphous Si/SiO₂⁴² and sapphire⁴³ the correlation length was largest on the amorphous surface. The longest vertical crystalline lengths, l/L , were observed on water and sapphire and the shortest on Si/SiO₂ and this reflects the nature of the interaction between the head group and substrate.

Table 2: GID and BR derived real space parameters, ξ and l/L , for C_n -TS and previously published results for similar systems.

Molecule	Substrate	ξ (Å)	l/L (%)
C_n -TS	Si/SiO ₂	50–66	47
OTMS	Water	35–80	-
C ₁₈ OH (SF)	Si/SiO ₂ ⁴²	350	72
	Sapphire ⁴³	200	75–90
C ₁₈ OH (LF)	Water ^{53–55}	> 2500	90
C ₁₈ (SF)	Own melt ^{33,47}	> 9000	90

C_n -TS and OTMS head groups undergo a partial condensation reaction with their lat-

eral neighbors, resulting in a partial Si-O-Si cross-linked network. In the case of a solid, hydroxylized, substrate, such as Si/SiO₂ or sapphire, a partial condensation reaction with the substrate additionally occurs, yielding a Si-O-Si surface bond. These bonds have a combined length of $\approx 3.4 \text{ \AA}$ ³⁶ and are hence smaller than the vdW diameter of a single hydrocarbon chain of $3.50 \text{ \AA}$.³ Further, this bond length is significantly smaller than the lattice constant of $a_{\text{Cn-TS}} \approx 4.82 \text{ \AA}$, as measured with GID. Due to this size-mismatch, the lateral coherence lengths is limited to a few tens of Ångstroms for both these cross-linked systems, and for OTMS a direct connection between number of cross-links and coherence length could be extracted by using different pH values in the underlying water surface.⁵² This similarity suggests that the limited domain size originates in the additional length scale introduced by the cross-links and is not caused by the chemical attachment to the substrate.

For alcohol monolayers, on the other hand, the linker group is a hydroxyl group, which binds to the surface solely via a hydrogen bond. Since the lateral order for all systems is a complex interplay between this linker-group-substrate interaction and the vdW interaction between the hydrocarbon chains, these differences will manifest in the in-plane packing. For instance, on sapphire, where the lattice-match between monolayers and the substrate promotes pseudo-rotational epitaxy (C18-TS)²⁷ or epitaxy (alcohols),⁴³ the in-plane symmetry of the substrate and the monolayers is hexagonal. This is to be compared with amorphous and liquid supports such as Si/SiO₂ and water which do not provide an ordering field for the monolayer. Despite this, the in-plane symmetry is still hexagonal with a similar lattice constant. This suggests that for these systems (and other similar systems of closely packed alkyl-chain films) the in-plane structure is dominated by the chain-chain interactions and independent of the headgroup-substrate interactions.

The reduced vertical crystallinity found for SAMs can result from Gauche defects or twists in the dihedral angles where the latter carries a smaller energy penalty. It is known from FTIR studies that C18-TS SAM chains comprise a significant chain-end gauche defects, which destroy rotational symmetry. We expect that this would reduce the vertical crystalline

length by about $1-2 \text{ \AA}$ and this explains the slightly reduced lengths for alcohols on sapphire and the free surface of alkanes but is incapable of explaining why $\sim 12 \text{ CH}_2$ groups in the alkyl chain of C_n -TS do not contribute to the crystallinity. The fact that the vertical crystalline length, l , is nearly equal for C18-TS on amorphous Si/SiO₂ and the nearly commensurate sapphire substrate²⁷, suggests that the strain induced by the lateral Si-O-Si cross-linkages is more relevant than the underlying symmetry of the substrate. As a result of the size-mismatch induced interfacial strain, the region of the alkyl chains near the head group must contain a significant number of twisted dihedral angles which reduces the crystallinity in the near surface region. The distortions caused by the covalent Si-O-Si bonds are relatively strong compared with the weak hydrocarbon chain interactions and the reduced crystalline vertical length at the interface, ~ 11 carbon atoms, is a consequence of the strain. This length is derived from the intercept, 12 ± 1 shown in Fig. 5 where we also account for the disordered terminal methyl group.⁵⁶ We note that we are unaware of BR measurements for OTMS on water.

In more weakly bound monolayers, e.g. alcohols on solid and liquid supports, the reduced vertical crystallinity can be rationalized as follows. On solid substrates, strain is introduced in the case of amorphous Si/SiO₂, since the molecules' head-groups are pinned to fixed, but randomly distributed sites ($l/L \approx 65\%$).⁴² On the disordered water surface on the other hand, the liquid substrate and the mobility of the head groups do not induce such steric distortions and hence the vertical crystallinity ($l/L \approx 90\%$) is only limited by the gauche defects and twisted dihedral angles at the ends of the chain, as predicted by a mean field statistical model.⁵⁷ A sketch of the observed phenomena for C18-TS on Si/SiO₂, is shown in Fig. 6. We emphasize that this structural picture is in reasonable agreement with recent infrared spectroscopy results showing the existence of enhanced surface disorder.^{22,49}

Interestingly, Vibrational Sum Frequency Generation Spectroscopy measurements and molecular dynamics (MD) simulations of n -alkyl phosphonic acid (C_n -PA) SAMs⁵⁸, showed a similar change in the SAM morphology from an amorphous phase (C6-PA, C10-PA) to a

Figure 6: Model for partial vertical crystallinity in a C18-TS monolayer on Si/SiO₂ and the strains leading to this behavior, as discussed in the text.

slightly denser, crystalline phase (C14-PA, C18-PA) with increasing chain length, which was attributed to the larger space occupancy of the PA head group as compared to the alkyl chain. As is the case in our present study, the increase in density with n appears as a small effect. Furthermore, it is worth noting that Prasad et al.⁵⁹ have observed a similar effect of partial crystallinity in surface-frozen monolayers of poly(n -alkyl acrylate)s, and they have attributed this to steric hindrance near the polymer backbone. Finally, a qualitative analysis of Yamamoto et al.⁶⁰ by MD obtained structures of C18-TS on Si/SiO₂ along the surface normal supports our finding of a partial vertical crystallinity.

Conclusion

In conclusion, we have shown that C_n -TS SAMs on Si/SiO₂ consist of vertically aligned and laterally hexagonally packed molecules with the exception of C12-TS, which appears liquid-like. For C18-TS and C22-TS the packing density is close to that expected for a rotator phase and for smaller chain lengths the density is less, thus suggesting a more disordered structure.

Furthermore, we have elucidated how the strain in *Cn*-TS SAMs on Si/SiO₂ originates from the size mismatch between the head group and the chain regions and how this translates into the SAM’s structural properties. Our results shows that there must be disorder along the chain and that the ~ 11 CH₂ units near the substrate do not contribute to the crystallinity. This is consistent with our observation that the vertical crystallinity increases linearly with *n*. We suggest that the imposed steric hindrance of the head group bonding also gives rise to the limited in-plane coherence length of ~ 60 Å. Finally, our results show that C18-TS exhibits the highest electron density, largest crystalline coherence length and is the most extended of the four molecular lengths investigated in the present study. This finding validates why C18-TS is widely used to form Self-Assembled Monolayers.

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Graphical TOC Entry