

Evidence for a Unique Chain Organization in Long Chain Silane Monolayers Deposited on Two Widely Different Solid Substrates

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We address the longstanding issue of substrate effects in alkylsiloxane monolayer self-assembly. With proper substrate prehydration, we observe formation of identical quality, compact, quasi-crystalline monolayers on oxidized silicon and gold substrates with widely different chemical character, the former capable of covalent bonding to the adsorbed molecules via silanol groups and the latter devoid of reactive surface sites. Infrared spectroscopy, ellipsometry, and wetting measurements show identical average film structures consisting of highly extended chains tilted at $10 (\pm 2)^\circ$ with significant end-*gauche* defect content. This observed substrate independence is consistent with our previous hypothesis that substrate-bound water promotes the decoupling of the organic film from the underlying solid surface.

Deposition of stable, low defect, hydrophobic monolayers,^{1,2} on solid substrates is of significant interest in a wide variety of applications ranging from electronics³ to biological interfaces.⁴ One of the most popular methods involves the use of solution self-assembly of long-chain alkyltrichlorosilanes (silanization) to form densely packed, highly organized, monolayer films. This simple technique was proposed almost 50 years ago by Zisman⁵ and advocated subsequently by Sagiv.⁶ The fact that many different preparation protocols have been reported in the literature suggests, however, a lack of general understanding of the precise mechanism controlling the deposition process. Recently, a unifying mechanism has been proposed^{7,8} which explains why the presence of a substrate-bound water film⁹⁻¹¹ and the control of the deposition temperature below a threshold value¹² are necessary in order to obtain high-density, Langmuir-like film structures. The crux of the argument is that one should decouple the monolayer film from the substrate structure as much as possible in order to allow for the in-plane lateral reorganization of the physisorbed molecules. This mech-

anism forces into question the widely held structural picture of these films in which direct covalent bonding (cross linking or grafting) between adsorbate molecules and reactive substrate groups is necessary for stable film formation^{6,13-16} and in which the role of water is portrayed simply as a source for hydrolysis of the trichlorosilane head groups. In order to resolve this issue, we have quantitatively characterized the structures of monolayers of octadecylsiloxane (ODS) prepared on prehydrated surfaces of oxidized silicon (SiO₂/Si) and gold. These two substrates have opposite chemical characters in that the former bears a high density of surface reactive groups (~ 5 silanols ($=\text{Si}=\text{OH}$)/nm²)¹⁷ capable of chemically reacting with the hydrolyzed silane molecules whereas the latter is chemically inert and incapable of permanent surface bonding.

The ODS monolayers were formed by rapid immersion of the cleaned, bare, substrates in octadecyltrichlorosilane [CH₃(CH₂)₁₇SiCl₃; OTS] solutions according to a previously reported procedure which requires careful control of the reaction temperature and substrate hydration conditions.^{7,8} This approach has been shown to produce near-limiting critical surface tension values for SiO₂ substrates.^{7,8,12} Prior to self-assembly, SiO₂/Si surfaces were hydrated by exposure to a water vapor atmosphere. Previous studies of water adsorption on quartz have shown that a water layer of ~ 15 – 20 Å thickness forms spontaneously over a broad range (10–85%) of relative humidity.¹⁸ Therefore, we believe that several monolayers of water at the surface of SiO₂/Si wafers are present just prior to the film deposition. Recently Vigil and co-workers¹⁹ have given a more detailed description of this aqueous layer in terms of a hygroscopic network of silanol and silicic acid chains in which the water retains its mobility beyond the first ~ 3 Å layer bound to the

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substrate.²⁰ In order to make Au surfaces wettable by water, they were activated^{12,21} using UV-ozone exposure²² to form a transient AuO_x monolayer, whose presence was shown by X-ray photoelectron spectroscopy (XPS) analysis. Water then was deposited by spin-coating and the hydrated sample quickly immersed in the OTS solution. Because the hydrophilic AuO_x layer is quite unstable toward disproportionation back to bare gold, any delays in sample immersion result in poor quality, lower, coverage films. In the case of good films, XPS analysis showed complete absence of gold oxide after preparation. Finally, improper substrate hydration always gave erratic, unsatisfactory results.

Measurements of ellipsometric film thicknesses^{2,23} (measurements at 632.8 nm and 70° incidence; calculations via a rigorous anisotropic model⁸ with $n_x = n_y = 1.484$ and $n_z = 1.559$) resulted in a single value of 25.2 ± 1 Å for the ODS films on both Au and SiO₂/Si substrates. Assuming a 26.2 Å length for an all-*trans* extended ODS molecule,¹³ the coverage equivalent to the previous thickness is $\sim 96 \pm 4\%$ of the theoretical maximum coverage for a single monolayer based on a limiting density equal to crystalline polyethylene. Similarly, measurements of the critical surface tensions (γ_c) of the monolayers on the two different substrates also resulted in a single value of $\gamma_c = 20.5 \pm 0.5$ dyn cm⁻¹. The measurement was done using contact angles of sessile drops of a series of liquid *n*-alkanes of known surface tensions from *n*-decane to *n*-hexadecane according to the linear extrapolation method of Zisman.²⁴ The observed value of γ_c agrees precisely with that purported for a surface of methyl groups with near-limiting density.^{7,8,25} The above two results demonstrate that films with apparently identical macroscopic properties and at near-maximum surface coverage can be obtained reproducibly on substrates of a widely different nature. However, the above data reveal little of the structural aspects of the film. We have derived this information from an incisive quantitative, analysis of infrared vibrational spectra which yields the average chain conformational and orientational order.

The IR spectra were obtained in transmission at normal incidence for the ODS films on SiO₂/Si substrates and in p-polarized reflection at an 86° angle of incidence for the ODS films on gold.²⁶ Freshly cleaned, substrates were used prior to silanization to collect reference spectra.

The solid traces in parts A and B of Figure 1 correspond to the experimental C-H stretching mode spectra of ODS films on hydrated SiO₂/Si and hydrated Au surfaces, respectively. While the two spectra are markedly different, we will show below that they represent essentially

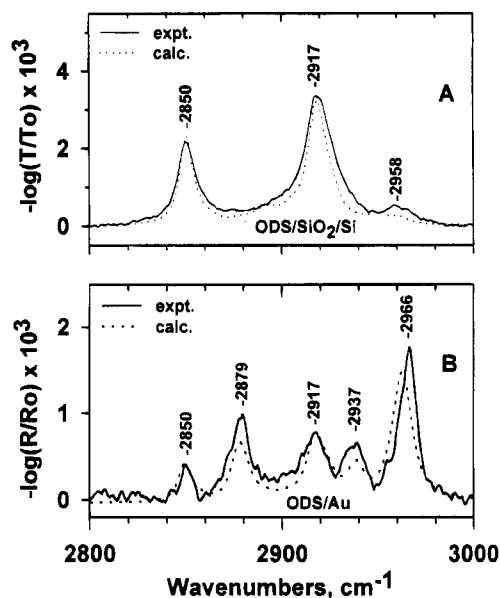


Figure 1. Infrared spectra of ODS monolayers in the C-H stretching mode region (2800–3100 cm⁻¹): (A) transmission spectra of films deposited on hydrated surfaces of SiO₂/Si; (B) reflection spectra of films deposited on hydrated surfaces of Au. The solid line spectra represent experimental data and the dotted lines simulated spectra.

identical film structures. The peaks at 2958 cm⁻¹ in Figure 1A and those at 2879, 2937, and 2966 cm⁻¹ in Figure 1B are assigned to CH₃ group modes. The common peaks observed at 2850 and 2917 cm⁻¹ are assigned to methylene symmetric (d⁺) and antisymmetric (d⁻) stretching modes, respectively. The coincidence of these peak positions for the two monolayers indicates a common average conformational state. Since the peak positions for d⁺ and d⁻ modes of alkyl chains are reported typically to be in the range 2846–2850 and 2915–2918 cm⁻¹ for all-*trans* extended chains²⁷ and at ~ 2856 and ~ 2928 cm⁻¹ for liquid-like disordered chains,²⁸ we conclude that the chains are predominantly in the all-*trans*, extended conformation on both substrates. Similar all-*trans* chain conformation has been concluded in several previous studies,^{10,14,15,21,29} but the reported d⁻ peak frequency values are at least ~ 1 cm⁻¹ higher than the presently observed values. This indicates better conformational ordering and attendant higher molecular organization in the present films.

The dashed lines in Figure 1 correspond to best-fit, simulated spectra based on an extended alkyl chain

(20) One should note that while the characteristics of a highly hydrated substrate surface such as SiO₂ may be well-defined under the near-equilibrium conditions of water vapor exposure, once the substrate is immersed in the hydrocarbon silanization solution the character of the adsorbed water film becomes extremely dynamic because of the onset of consumption via exothermic Si-Cl hydrolysis, production via subsequent RSiOX condensations, and continual liquid phase/substrate surface partitioning. Partitioning of adsorbed water to hydrocarbon solvent is expected to be slight for SiO₂ surfaces since the threshold for thermal desorption of the adsorbed water in a vacuum environment is ~ 150 °C with $10 \leq \Delta H_{\text{ads}} \leq 20$ kcal·mol⁻¹ [e.g., see Iler, R. K. *The Chemistry of Silica*; Wiley: New York, 1979. Hair, M. L.; Hertl, W. J. *J. Phys. Chem.* **1969**, *73*, 4269–4275] and the water solubility in hexadecane is quite low. Experiments to monitor the exact water coverage at substrate surfaces using *in-situ* infrared spectroscopy, spectroscopic ellipsometry, and surface plasmon resonance are in progress.

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(26) Measurements made using an air-purged Fourier transform infrared spectrometer (Bomem Model MB-100, Québec, Canada) employing an unpolarized incident beam. The beam diameter was maintained at 6 mm by placing an aperture in front of the sample. Fringing effects were minimized by use of wedged Si wafers (Harrick Scientific, Ossining, NY). Reflection spectra were collected using an air-purged (CO₂, H₂O free), custom-modified Digilab FTS-60 Fourier transform infrared spectrometer (Bio-Rad, Cambridge, MA). The incoming IR radiation was focused on the sample with $\sim f/20$ optics and the reflected beam was detected using a narrow-band mercury-cadmium-telluride (MCT) detector cooled with liquid nitrogen. A wire-grid polarizer was placed immediately before the sample and oriented to give p-polarization. All reported spectra were obtained by co-adding multiple scans collected at 2 cm⁻¹ resolution. The interferograms were Fourier-transformed with triangular apodization and with zero filling in order to increase the spectral point density to give ± 0.3 cm⁻¹ errors in point positions. Spectral intensities are reported in absorbance units: $-\log(T/T_0)$ for transmission and $-\log(R/R_0)$ for reflection, where R_0 and T_0 are the reflectivities and transmissivities of the corresponding reference samples, respectively.

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structure with a 10° tilt (ϕ_{tilt}) of the long-molecular axis from the surface normal and a twist (ϕ_{twist}) of 46° of the C-C-C plane about its long axis (where $\phi_{\text{twist}} = 0$ corresponds to the CCC plane perpendicular to the surface plane). The assumed model of a rigid linear chain is justified by the above observation of predominantly all-*trans* conformations and will be confirmed below by the low-frequency spectra. The spectra were simulated according to methods derived previously.³⁰ The sample structures were modeled as {air/ODS/SiO₂/Si/SiO₂/ODS/air} and {air/ODS/Au}, corresponding to the experimental configurations. In all cases, the exact geometry of the experiment was incorporated in the simulation and the individual layer thicknesses were taken from the ellipsometry data. The optical function spectra for Au, SiO₂, and Si were obtained from the literature³¹ while those for a conformationally ordered ODS layer were obtained in an independent study.³² Spectra were simulated for a variety of trial chain orientations and the final one was selected on the basis of the best intensity fit³³ of the d^+ and d^- peaks to the experimental spectrum. This procedure yields the same average values of $10 (\pm 2)^\circ$ and $46 (\pm 2)^\circ$ for ϕ_{tilt} and ϕ_{twist} on both substrates. This coincidence of values is accurate within the stated error range.³⁴ An important point is that the CH₃ mode intensities, which appear *distinctly different* for the two substrates, are reproduced reasonably well by the simulation. The discrepancies in peak positions of the CH₃ features at 2958–2966 cm⁻¹ are not unexpected since these contain two modes (in- and out-of-plane asymmetric stretches) which appear at different frequencies and their quantitative behavior in monolayer assemblies is not well understood.³⁰ The critical conclusion from the above C-H mode analysis is that starting with a single set of optical function spectra, a single, unique tilted structure is obtained for the ODS films on the two substrates, within experimental error.

Further qualitative details of the monolayer structure can be obtained from the IR spectra in the 900–1500 cm⁻¹ range, shown in Figure 2. A series of peaks observed between 1150 and 1300 cm⁻¹ is well-resolved for films on Au (Figure 2B) but is absent for the SiO₂ substrates (Figure 2A). These features are assigned to a progression of coupled CH₂ wag modes³⁵ whose appearance is evidence for an all-*trans* chain conformational sequence in the alkyl chains. The peaks exhibit an average regular spacing of ~ 20 cm⁻¹ which is close to the value of 18 cm⁻¹ predicted^{27a} for a X-(CH₂)₁₇CH₃ all-*trans* sequence, where X = SiO_x in the present case. The slightly higher observed spacing indicates the presence of disorder at the last one or two

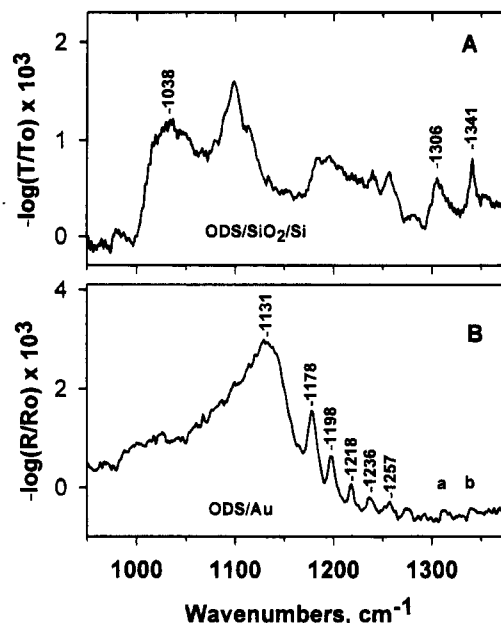


Figure 2. Infrared spectra of ODS monolayers on the hydrated surfaces of SiO₂/Si and Au in the 950–1550 cm⁻¹ frequency region (spectral details are explained in Figure 1).

CH₂ groups of the chain terminus at the ambient interface. Such disorder is not unexpected since both the ellipsometric coverage and average tilt angle indicate slightly incomplete packing and the disorder will tend to concentrate at the chain terminus where more mobility exists. Unfortunately, the surface IR selection rule precludes observation of the wag progression in transmission,³⁶ consistent with its absence in Figure 2A, and thus analysis of these modes is not possible with the ODS/SiO₂/Si samples. However, the weak peak observed at 1341 cm⁻¹ in Figure 2A can be assigned to a localized wag mode arising from an end-*gauche* chain defect (*tg*).³⁷ This evidence shows a similarity between the film defect structures on the SiO₂ and Au substrates and suggests that the very weak peak, marked b in Figure 2B and located at 1341 cm⁻¹ also, may be due to the end-*gauche* mode. Finally, the weak, asymmetric band at 1306 cm⁻¹ in Figure 2A for the SiO₂ substrate case, is reminiscent of a *gtg'* chain kink defect mode.³⁷ It is possible that peak a at ~ 1311 cm⁻¹ in Figure 2B for ODS/Au may also mark a *gtg'* kink defect but its intensity is too slight to be definitive. The appearance of such *gtg'* defects presumably occurs near the film surface and their presence shows again that the chain packing has not approached the theoretical limit.

The major conclusion from the above analysis is that the ODS films on Au and SiO₂/Si appear strikingly similar in terms of molecular-level detail. On the basis of the widely different chemistry of these two substrates, this result seems quite unexpected. Since permanent chemical bonding of the ODS species to the Au surface cannot occur,

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(31) *Handbook of Optical Constants of Solids II*; Palik, E. D., Ed.; Academic: Orlando, FL, 1985.

(32) The optical tensor contributions of individual vibrational modes were determined by analysis of the transmission spectra of pressed disks of KBr dispersions of polycrystalline samples of hydrolyzed OTS. The latter compound is a crystalline polymer with the general formula of [C₁₈H₃₇SiO_x(OH)_y]_n and details of its preparation and structure will be reported elsewhere (Parikh, A. N.; Schivley, M. A.; Allara, D. L., manuscript in preparation). Of a number of reference compounds investigated, this was by far the closest in terms of a structural match to the ODS monolayers.

(33) One can note that the simulated d^- mode bands in Figures 1B and 2B have slightly narrower line widths than the experimental bands. This reflects the fact that the polycrystalline, hydrolyzed OTS, used as the reference state, is slightly more ordered than the actual ODS monolayer. See footnote 32.

(34) For example, in the case of gold substrates, a change of ϕ_{tilt} from 10 to 5° drops the calculated d^+ and d^- absorptions below the noise level in the experimental spectra ($< 2 \times 10^{-5}$ absorption units). Similarly, a change of ϕ_{twist} from 46 to 52° results in a very conspicuous change in the d^+ to d^- intensity ratio from ~ 1.9 to ~ 2.8 .

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(36) The surface electric field of the IR radiation is perpendicular to the surface in the case of the reflection experiments on Au while the field is parallel to the surface in the case of transmission at normal incidence. Since the transition dipole moment of the chain wag modes is parallel to the chain axis and the chains are tilted near normal to the surface, the wag intensities can be expected to be severely reduced in transmission relative to reflection. In general, extension of these principles to transition dipoles oriented at intermediate angles to the surface normal means that the associated intensities will vary in magnitude between transmission and reflection depending upon the specific orientation (for example, see ref 30).

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the above conclusion implies that there must be *insignificant bonding in the case of ODS on SiO₂*. This conclusion follows from the simple consideration that the reactive silanol groups on the amorphous SiO₂ surface are *randomly distributed* and thus an increasing fraction of chain attachments at these silanol sites will force the film into an *increasingly disordered* structure.

Finally, we consider the 1000–1150 cm⁻¹ region where broad, complex bands are observed. These bands can be assigned straightforwardly to Si–O–Si antisymmetric stretching modes³⁸ and their presence indicates that cross-linking has occurred between the head groups of the physisorbed silane molecules. Such polymerization is not surprising since the average distance between the centers of mass of alkyl chains in their close-packed crystalline state is close to the natural Si–O–Si bond length.³ Therefore, condensation reactions between the –Si–OH groups of the trihydroxy head groups belonging to neighboring molecules is topochemically favorable. The end product then appears to be a comb-shaped polymer

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with a siloxane backbone and C₁₈ hydrocarbon side chains. At present, we cannot interpret these spectra quantitatively, as with the chain spectra, but such an analysis is in progress in order to assess the degree of polymerization and the molecular weight of these polymers.

In conclusion, this study shows that proper substrate hydration is the fundamental basis of strategies for the deposition of dense-packed, highly organized, long chain alkylsiloxane monolayers of similar structure on solid substrates of widely different chemical characters. In the absence of such hydration, the film cannot be decoupled from the substrate chemistry and in most cases, especially with reactive amorphous oxides, increased film defect content can be expected. However, we also point out that such bonding can confer additional film adhesion. Control of this surface bonding thus will allow the the engineering of films with controlled defect structures and stabilities.

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