THE STRUCTURE AND REACTIVITY OF ALKYLSILOXANE MONOLAYERS FORMED BY REACTION OF ALKYLTRICHLOROSILANES ON SILICON SUBSTRATES

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The Structure and Reactivity of Alkylsiloxane Monolayers Formed by Reaction of Alkyltrichlorosilanes on Silicon Substrates

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Abstract

Long-chain alkyltrichlorosilanes, $Cl_3Si(CH_2)_nX$, adsorb from solution onto silicon-silicon dioxide (Si/SiO_2) substrates and form ordered alkylsiloxane monolayer films. These films were characterized by wettability, ellipsometry, and XPS. Except for very short chains ($n = 0,1,2$), the wetting of these monolayers was approximately independent of chain length. The presence of small amounts of water was necessary for the formation of these films. The alkylsiloxane monolayers were stable in common organic solvents, water, and acid, but were destroyed by prolonged exposure to base. Simple reactions on vinyl-terminated monolayers generated alcohol-, carboxylic acid-, and bromine-terminated films whose contact angles were lower than the starting monolayers, but whose lengths were largely unchanged. Measurements of the contact angle of acid-terminated interfaces as a function of pH indicated that ionization of the surface-immobilized acids required stronger base than does ionization of soluble carboxylic acids. Monolayers containing mixtures of methyl- and carboxyl-functionalities exhibited wetting properties that mirrored the composition of the interface.

Introduction

This paper describes the preparation of organic monolayer films by adsorption and reaction of alkyltrichlorosilanes on silicon-silicon dioxide (Si/SiO$_2$) substrates, the characterization of these films, and the correlation of the molecular structure of the organosilicon compounds with the macroscopic properties (e.g. wettability) of the monolayers derived from them. The formation of organic monolayers from organosilicon compounds on appropriate substrates (particularly on glass and on the native surface oxide layer of silicon)[1-7] is one of several methods for forming organic monolayers. Others include the adsorption of alkyl thiols,[8-14] dialkyl disulfides,[15-17] and dialkyl sulfides[18,19] on gold, fatty acids on alumina,[20-22] and alcohols and amines on platinum.[23]

Because the organosilicon-derived monolayers are physically robust, they are widely used in technology.[24,25] The studies of Sagiv and coworkers have established that monolayers derived from long-chain n-alkyltrichlorosilanes are highly ordered.[1-6] Our examination of these systems had two objectives. First, we wished to compare the properties of these films with those of analogous monolayers formed by other methods. Second, we intended to examine simple organic reactions occurring in these monolayers, and to use these reactions to characterize the chemical environment within the monolayer.

The alkyltrichlorosilanes used here had the structure $Cl_3Si(CH_2)_nR$ (Figure 1). The extent to which the group R is segregated at the solid-vapor (or solid-liquid) interface depends on the degree of order within the monolayer.

We wished to compare monolayer films that differed primarily in the polarity of the group R. Many polar groups (i.e. R = $-CH_2OH$, $-CO_2H$) are, however, incompatible with the trichlorosilane group. We therefore generated such polar functional groups from non-polar precursors (especially R = $-CH=CH_2$) after formation of a monolayer film of the latter. Sagiv and coworkers have used similar strategies.[5,26-28]

This investigation relied heavily on comparisons of X-ray photoelectron spectroscopy (XPS), ellipsometry, and wettability. Our work and that of others has shown that wetting is one of the most surface sensitive techniques currently available.[29-31] XPS and ellipsometry provide information averaged over the entire thickness of the monolayer (although XPS is certainly more sensitive to the organic groups close to the monolayer-air interface than to those near the silicon dioxide-monolayer interface).[32,33]

Results

Preparation of Alkyltrichlorosilanes. We synthesized alkyltrichlorosilanes using two procedures (Scheme I). Method A involved reaction of a Grignard reagent with tetrachlorosilane[34] and was used primarily for silanes containing a terminal vinyl group. Method B used the

platinum-catalyzed addition of trichlorosilane (HSiCl$_3$) to a double bond[35] and provided a practical route to saturated trichlorosilanes and alkyltrichlorosilanes containing a terminal ester. NMR spectroscopy suggested that the purities of these compounds were greater than 97% and that the impurities which we could detect did not contain the -SiCl$_3$ group.

Preparation of Monolayers. Monolayers were prepared on clean silicon wafers, whose surface is believed to be silicon dioxide,[36] with ~ 5 x 10^{14} -SiOH groups per cm^2.[37] The substrate was immersed in an unstirred solution of the alkyltrichlorosilane in hexadecane or bicyclohexyl (1-25 mM) for 1 - 24 h. The wafer was then removed from the solution, rinsed with organic solvents, and dried. The substrate was typically exposed to the air for ten minutes before immersion. During this period the ellipsometric angles for the substrate were measured. The substrate was then transferred into a dry, nitrogen atmosphere.

Because of the susceptibility of the silicon-chloride bond to hydrolysis, it was necessary to limit the amount of water present in the system in order to obtain monolayers of good quality. Exceptional care (of the level used in handling organolithium reagents) was, however, not necessary. The surface of the silicon/silicon dioxide substrate was certainly not anhydrous,[38-40] and a thin film of surface-condensed water may be necessary for the formation of the monolayer. Although these monolayers were usually prepared

while keeping the solution of alkyltrichlorosilane under a nitrogen atmosphere, they could also be formed under ambient laboratory conditions when the relative humidity was less than 40%. When stored under nitrogen, the solutions for the formation of the monolayers could be used for several weeks. When stored in the laboratory atmosphere, the solutions were used within 12 hours; after 24 hours a visible precipitate often formed.

Monolayers composed of methyl- and vinyl-terminated alkylsilanes were the easiest to form. These monolayers were autophobic to the hydrocarbon solution; that is, they emerged uniformly dry from the solution. Monolayers having terminal ester groups emerged wet from the solution used in their formation. Unfortunately, if the alkyltrichlorosilane in the solvent adhering to the substrate was exposed to water, a cloudy film deposited on the surface, presumably due to the formation of a gel of polymeric siloxane. Removal of this film by washing was impossible, although it could apparently be largely removed by actually wiping the surface with a tissue or swab.[41] We therefore prepared these films from dilute (0.1 mM) solutions in methylene chloride or carbon tetrachloride in order to minimize the amount of alkyltrichlorosilane that was left on the surface. These monolayers were rinsed with methylene chloride before exposure to the ambient atmosphere.

Contact Angles. The techniques used to measure contact angles have been described elsewhere.[29] These

measurements were routinely made with deionized water (pH = 5.6) and with hexadecane. The values reported are the usual quasi-equilibrium static advancing angles, θ_a.[29]

Most discussions based on measured contact angles begin with Young's equation (eq 1).[29,42] Here the γ's represent the

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv}\cos\theta \qquad (1)$$

surface tensions (or energies) of the solid-vapor (sv), solid-liquid (sl), and liquid-vapor (lv) interfaces. The free energies of the interfaces are related to $\cos\theta$ rather than to θ. We note that Young's law is an exact thermodynamic relationship only for systems at equilibrium.[42] All of the systems that we studied exhibited significant hysteresis[43] in the measured advancing, θ_a, and receding, θ_r, contact angles of water ($\theta_a^{H2O} - \theta_r^{H2O} \approx 10°$ [at $\theta_a^{H2O} \approx 110°$], 12 [at $\theta_a^{H2O} \approx 70°$], and 20° [at $\theta_a^{H2O} \approx 34°$]), and are thus not at equilibrium. This hysteresis is approximately constant in terms of energy (that is, the value of $\cos\theta_a - \cos\theta_r \approx 0.2$ is constant).

Figure 2 presents θ_a for monolayers prepared from a homologous series of methyl-terminated alkyltrichlorosilanes. Our values of θ_a^{H2O} agree with those reported by Sagiv.[1] Values of θ_a^{HD} are slightly lower than those of Sagiv, but agree with the values of Ulman et. al.[44] Values of θ_a^{H2O} were consistently less (3 - 6°) than the corresponding values on self-assembled monolayers of n-alkyl thiols on gold.[11] There

was no alternation in θ_a^{HD} for alkylsilanes having odd and even numbers of carbon atoms. Such alternation has been reported for monolayers of n-alkyl carboxylic acids on alumina[20] and, to a smaller extent, for alkyl thiols on gold.[11]

The contact angle of hexadecane on surfaces prepared from methyltrichlorosilane (CH_3SiCl_3) was anomalous. While these films were probably not monolayers (see below), the observed contact angle was higher than that on monolayers prepared from ethyl- and propyltrichlorosilane. Polysiloxane films prepared from $CH_3Si(CCH_3)_3$ have a lower critical surface tension (and thus a higher contact angle) than films prepared from the corresponding ethyl compound.[25]

Ellipsometry. Figure 2 presents the thicknesses estimated by ellipsometry[45,46] for a homologous series of methyl-terminated alkylsiloxane monolayers. We have compared these thicknesses with values estimated by low-angle X-ray reflection and found excellent agreement.[47,48] The X-ray measurements also demonstrated that these structures were actual monolayers rather than a mixture of uncovered and multilayer regions. We believe that these ellipsometric thicknesses have an uncertainty of $\pm$ 2 Å.[49,50]

The data are remarkably consistent: for a given alkyl group, the thicknesses measured on different Si/SiO$_2$ substrates fall within a 5-Å range. These estimated thicknesses correspond well to a model for the monolayer having the n-alkyl chain in the all-trans conformation and

oriented nearly perpendicular to the surface (Figure 1).[51] For a _trans_-extended chain the projection of the carbon-carbon bond onto the surface normal (z axis) is 1.26 Å.[52] For the C-Si and Si-O bonds the projections are 1.52 and 1.33 Å respectively. Including an additional 1.92 Å for the terminal methyl group,[53] we expect a monolayer prepared from octadecyltrichlorosilane (OTS) to have a thickness of 26.2 Å. The observed range of 22.6 to 27.6 Å (Figure 2) brackets this value.

The length (L) of a methyl-terminated monolayer containing n methylene units should have the dependence given by equation 2. A best fit to the experimental data for

$$L = 1.26n + 4.78 \qquad\qquad (2)$$

n = 1 - 17 has a slope of 1.26 Å per methylene unit and an intercept of 4.02 Å.[54,55] We therefore concur with previous studies based on infrared spectroscopy[1,44] that the alkyl chains in these monolayers are _trans_-extended and that any tilting of the chains with respect to the normal axis is small.

X-ray Photoelectron Spectroscopy (XPS). The survey spectrum for a monolayer prepared from OTS (Figure 3) showed only three elements: silicon (2s, 150 eV; 2p, 99 eV)[56], carbon (1s, 285 eV),[57,58] and oxygen (1s, 532 eV; 2s, 23 eV; Auger-KLL, 977 eV).[56] The spectra distinguish between the bulk silicon (2s, 150 eV; 2p, 99 eV) signal and that due to

the surface oxide (2s, 154 eV; 2p, 103 eV).[59] The peaks at 116, 133, 166, and 183 eV are subsidiary peaks of the silicon resulting from energy loss to the bulk plasmons of the substrate.[60,61] As the angle between the plane of the electron detector and the normal to the surface (takeoff angle) decreased (Figure 4), the intensity of the carbon signal increased relative to that of the signals of silicon and oxygen, the intensity of the oxygen signal increased relative to that of silicon, and the intensity of the silicon dioxide signal increased relative to that of bulk silicon. These observations are consistent with a model for the monolayer as a layer of hydrocarbon above a layer of silicon oxide, which in turn lies above bulk silicon.

XPS detected no chlorine in the monolayers, even for those derived from $Cl_3Si(CH_2)_nCH_3$, n=0,1. Its absence was thus due to its absence on the surface, rather than to attenuation of the chlorine signal by the hydrocarbon layer. Since there was no chlorine in the monolayer, each silicon atom from the starting alkyltrichlorosilane must have formed three silicon-oxygen bonds of some type (Figure 5). Studies on silicas indicate that the density of hydroxyl groups in the oxide does not exceed one group every 20 $Å^2$ [37,38,62] (approximately one for each exposed silicon atom). This density is not sufficient to support attachment of a monolayer entirely by Si-O-Si bonds between the organosilane and the substrate. We have found, using the technique of X-ray reflection, that the area per RSi- group in these

monolayers is 21 ± 3 Å^2.[47] Attachment of the silicon atom of the starting silane entirely to surface hydroxyl groups would require one -SiOH per 7 Å^2. We therefore conclude that water is involved in the creation of Si-O-Si bonds between the alkylsilane moieties of the monolayer and Si-OH bonds.[63-65] The rates of formation of these monolayers support this conclusion (vide infra).

Figure 6 presents the atomic ratio of carbon to the silicon substrate (C/Si$_{sub}$) as measured by XPS for monolayers prepared from saturated alkyltrichlorosilanes.[66] This ratio has approximately the expected exponential dependence on the thickness of the monolayer (see the supplemental material to this paper). This result demonstrates that the length of the monolayer as determined by ellipsometry correlates with the total number of carbon atoms in the monolayer.

The XPS spectra of monolayers prepared from CH$_3$SiCl$_3$ were, as in the contact angle measurements, atypical of alkylsiloxane monolayers. The intensity of the C 1s peak was 80-100% of that from monolayers prepared from ethyltrichlorosilane (CH$_3$CH$_2$SiCl$_3$), instead of the expected 50%. This result suggests that these structures were probably disordered bilayers, rather than monolayers.

Rate of Formation of Monolayers. Our objective in examining the rate of formation of these monolayers was primarily to determine conditions that yielded monolayers reproducibly. Figure 7 follows the formation of a monolayer prepared from tetradecyltrichlorosilane (TTS,

$CH_3(CH_2)_{13}SiCl_3)$. The length of the monolayer reached a plateau of 20 Å after ca. 40 minutes. This length was approximately that expected for a complete monolayer (21.1 Å).

Humidity influences the time needed to form a monolayer. When the monolayers were prepared by immersing the silicon wafer in a solution of alkyltrichloro-silane maintained under a dry atmosphere, a complete layer was obtained only after 5 hours; when the same experiment was conducted under air at 30% r. h., formation of the monolayer was complete in approximately 1 hour. We believe that this difference in rate was due primarily to different amounts of water adsorbed on the polar surface of the Si/SiO_2 substrate or otherwise available for the formation of Si-O-Si linkages.

Stability. After washing with ethanol to remove contaminants adsorbed from the air, samples of methyl-terminated silanes that had been stored for 18 months in closed containers under air had contact angles and lengths indistinguishable from those determined immediately after preparation. More polar surfaces contaminated more rapidly than non-polar ones, but even these could be cleaned by rinsing with ethanol. Rubbing the surface vigorously with a tissue or cotton swab did not change the thickness or wettability of the monolayer.

Monolayers prepared from $CH_3(CH_2)_{13}SiCl_3$ (TTS) were stable in contact with aqueous acid at room temperature and hexadecane at 75 °C (Figure 8). When exposed to aqueous base

at room temperature, approximately 50% of the monolayer had been removed after 80 min. While the substrate appeared normal at 80 min, after 160 min its surface was visibly etched. The negative length observed at this point probably was due to attack on the native oxide. Since the silicon-oxygen bond hydrolyzes under basic conditions,[67] this destruction of the monolayer is not surprising.

The resistance of the alkylsiloxane monolayers to desorption in hot hexadecane contrasts with the rapid desorption observed for alkyl thiols adsorbed on gold; hexadecyl thiol has a half-life for desorption of 30 minutes at 83 °C in hexadecane.[11] Thus the formation of alkylsiloxane monolayers is not the result of a partitioning of the constituent molecules between substrate-bound and solution phases. We presume that the formation of these monolayers is driven by the formation of the covalent silicon-oxygen bond, rather than by the maximization of van der Waals interactions between adjacent alkyl groups.

The etching of these monolayers in base was often heterogeneous. We sometimes observed etched surfaces containing patches in which the monolayer was apparently intact while in other areas the substrate had been visibly pitted. This result suggests that etching was initiated at defects in the film and proceeded through the creation of regions denuded of monolayer. This macroscopic heterogeneity demonstrates the presence of at least macroscopic islands, although it does not provide proof of the microscopic

structure of the monolayer. In contrast, incomplete monolayers, prepared by removing the substrate from the solution of alkyltrichlorosilane before the monolayer has completely formed, have a uniform, liquid-like structure.[47,48,68]

Reactions Involving the Terminal Vinyl Group. We generated alcohols and carboxylic acid groups from vinyl-terminated monolayers, using procedures similar to those developed by Sagiv.[5,26] Figure 9 presents the contact angles and ellipsometric thicknesses for three vinyl-terminated monolayers. Although the contact angles were uniformly lower than those of the corresponding methyl-terminated monolayers, both the contact angles and thicknesses mirror the trends observed for the saturated alkylsiloxanes.

Figure 10 summarizes the oxidation of the vinyl group of a monolayer prepared from 16-heptadecenyltrichlorosilane (HTS, $Cl_3Si(CH_2)_{15}CH=CH_2$) to a carboxylic acid by $KMnO_4$ and $NaIO_4$.[69,70] As expected, the surfaces became more hydrophilic as vinyl groups were converted to carboxylic acid moieties. The limiting value for the contact angle of water was $\theta_a^{H_2O} \approx 30°$. Ellipsometry demonstrated that neither the vinyl- nor the methyl-terminated monolayer changed in thickness during the reaction.[71] The change in contact angle was thus due to oxidation of vinyl groups, rather than to etching of the monolayer. The conclusion that the thickness of the monolayer was unchanged upon oxidation is reasonable. The reaction replaces the $-CH=CH_2$ group with a $-CO_2H$ group;

the change in length resulting from this reaction is less than the precision of ellipsometry. Figure 11 shows XPS spectra for a monolayer prepared from 10-undecenyl-trichlorosilane ($Cl_3Si(CH_2)_9CH=CH_2$) after oxidation. We were unable to detect the presence of manganese, iodine, potassium, or sulfur. Since the sensitivities of manganese and iodine are large in XPS (Mn $2p_{3/2} \simeq 7.2$ and I $3d_{5/2} \simeq 15.8$ relative to carbon[72]) we conclude that no residual oxidant remained on the surface. Although the sensitivities of S ($2s \simeq 1.48$) and K ($2p_{3/2} \simeq 2.15$)[72] are lower, there were no signals from these elements in the XPS spectrum. We have occasionally found sodium (up to a monolayer) or calcium (up to 0.2 monolayers). The exact form or source of these contaminating elements is unclear, although sodium was present in the oxidizing solution.[73]

The high-resolution C 1s spectrum for the vinyl group after oxidation clearly showed the appearance of a broad, new peak centered at 289.2 eV ($-\underline{C}O_2H$).[74] The main carbon peak also became asymmetric, presumably due to a small shift in binding energy for the carbon atom bound directly to the $-CO_2H$ group.[75] Although the oxygen atoms of the $-CO_2H$ group could not be distinguished from the SiO_2 background, the intensity of the oxygen signal had increased by 10 percent.

Figure 12 compares aqueous contact angles for the monolayers obtained by oxidation of C_6, C_{11}, and C_{17} vinyl-terminated monolayers. The contact angles of the acid

interfaces created by this process were approximately independent of the length of the silane.[76]

As a check on these results, we have used an alternative method for generating a monolayer having terminal carboxylic acids. We prepared a monolayer having terminal ester groups by adsorption of $Cl_3Si(CH_2)_{10}CO_2CH_3$ onto a silicon wafer. We then hydrolyzed the ester groups in this monolayer with concentrated aqueous HCl. The contact angle for the ester-containing interface was $\theta_a^{H_2O} = 73°$; that for the hydrolyzed, carboxylic acid-containing interface was $\theta_a^{H_2O} = 40°$. The corresponding contact angle for the interface prepared by oxidation of a monolayer of $-Si(CH_2)_9CH=CH_2$ groups was $\theta_a^{H_2O} = 34°$.

Although we cannot prepare siloxane monolayers terminated with carboxylic acids directly since $RSiCl_3$ and RCO_2H react, structurally well-defined carboxylic acid-terminated monolayers have been prepared by adsorbing alkyl thiols with terminal $-CO_2H$ groups, $HS(CH_2)_{10-20}CO_2H$, onto gold.[11] The contact angle of water on these monolayers, $\theta_a^{H_2O} = 0°$, is significantly lower than that on the corresponding siloxane films. We can estimate the amount of acid at the solid-water interface of the oxidized siloxane monolayer by using Cassie's assumption that the interfacial free energy of a mixed surface is a linear combination of the energies of the functional groups at the interface.[77,78] This estimate suggests that approximately 80% of the exposed interface consists of carboxylic acid, with the remainder

presumed to be hydrocarbon. Wetting alone, however, cannot distinguish between hydrocarbon remaining from incomplete oxidation of a highly ordered monolayer and hydrocarbon exposed in a disordered monolayer whose constiuent vinyl groups have been completely oxidized.[79]

We have examined two additional reactions involving the terminal vinyl group (figures 11 and 12). The first is the introduction of an alcohol group via hydroboration. Sagiv has successfully used this reaction for the creation of multilayer assemblies.[26-28] We observed θ_a^{H2O} = 45 - 55° for these ω-hydroxylated interfaces, in agreement with Sagiv. We conclude, by comparison with the analogous hydroxyl-terminated monolayers prepared by adsorption of ω-hydroxythiols on gold (θ_a^{H2O} = 0°),[11] that approximately 70% of the solid-water interface was hydroxyl groups. Ellipsometry indicated that the vinyl-terminated monolayers had thicknesses similar to those of the hydroxyl systems derived from them. XPS spectra of the oxidized monolayer (Figure 11) showed a new peak at 286.6 eV characteristic of a hydroxyl-substituted carbon atom. Survey spectra did not reveal surface contaminants, but the boron cross section is small (0.49 relative to carbon)[72] and occurs in the same region as the plasmons for Si 2s.

Additional evidence for interfacial hydroxyl groups was provided by trifluoroacetylation using trifluoroacetic anhydride. The contact angles of the resulting material (θ_a^{H2O} = 88°, θ_a^{HD} = 51°) were similar to those observed for

trifluoroacetate esters prepared from monolayers of
HS$(CH_2)_{11}$OH on gold (θ_a^{H2O} = 96°, θ_a^{HD} = 60°)[80] but lower than
those for monolayers prepared from Cl$_3$Si$(CH_2)_2(CF_2)_7$CF$_3$
(θ_a^{H2O} = 109°, θ_a^{HD} = 71°). The XPS spectrum (Figure 13)
showed the expected F 1s signal at 688.5 eV. The intensities
of the acid and trifluoromethyl species in the high
resolution C 1s spectrum were equal to that of the alcohol,
suggesting that this treatment had resulted in acylation of
all the alcohol groups in the interface. Exposing the vinyl-
terminated monolayers to the same reagent did not introduce
fluorine into the monolayer (Figure 13).

We have also allowed the vinyl-terminated monolayers to
react with Br$_2$ in a CH$_2$Cl$_2$ solution to generate terminal
-CHBrCH$_2$Br and related brominated groups (Figures 11 and 12).
This interface showed θ_a^{H2O} = 80°. Ellipsometry indicated
that the apparent length of the monolayer had increased
2 - 3 Å. Since the reaction introduces two bromine atoms,
each approximately the size of a methyl group, into the
layer, the observed change in monolayer length is reasonable.
XPS confirmed the presence of bromine in the surface
(Figure 11). The bromine was labile on exposure to X-rays
and the initial intensity of the Br 3d$_{5/2}$ and Br 3d$_{3/2}$ peaks
decreased by 10 - 15% in the time required to obtain
reasonable spectra.

Comparisons of the C 1s peaks in high-resolution XPS for
homologous monolayers terminated by -CO$_2$H, -CH$_2$OH, and

-CHBrCH2Br groups demonstrate that XPS can provide at least semiquantitative information concerning the relative quantities of functional groups in alkylsiloxane monolayers. For all three, as the number of methylene groups in the monolayer increased, the intensity of the peak due to the oxidized carbon atoms decreased relative to that of the unsubstituted polymethylene carbons (Figure 11). While the intensity of the carbon of the $-CO_2H$ group was difficult to quantify because of the breadth of the peak, the changes in intensity of the C 1s signals for the $-CH_2OH$ and $-CHBrCH_2Br$ groups were approximately those expected.

We have used the bromination of vinyl groups in an attempt to assess the extent of reaction of the $KMnO_4/NaIO_4$ and hydroboration oxidations. The carboxyl- and hydroxyl-terminated monolayers that resulted from these reactions on monolayers prepared from HTS were placed in a 1% solution of Br_2 in CH_2Cl_2 for 2 h. The XPS spectra for these monolayers, as well as the $-CHBrCH_2Br$-terminated interface prepared by reaction of the vinyl group with Br_2 alone, are shown in Figure 14. We note three features of these spectra. First, the brominated acid-terminated monolayer exhibited two bromine environments, one whose binding energy corresponds to $-CHBrCH_2Br$, the other shifted by ~ 1.8 eV to lower binding energy. We have tentatively assigned this new environment to $-CHBrCO_2H$, although the only evidence for this assignment is the absence of this signal in the brominated hydroxyl-terminated monolayer. Second, the amount of bromine in the

-CHBrCH$_2$Br environment for the acid was ~ 13% of that of the fully brominated interface; for the alcohol, the amount of bromine incorporated into the monolayer was ~ 7% of that of the fully brominated interface. Based on these spectra, we would conclude that the hydroboration reaction had proceeded to a greater extent than the permanganate-periodate oxidation. Although this conclusion is the opposite of that deduced from the contact angle data, these measurements may not be inconsistent. The assumption that the inherent wettabilities of alcohol- and acid-terminated monolayers are the same ($\theta_a^{H_2O}$ = 0°) is not necessarily correct. Furthermore, the contact angle measurements indicate which groups are in contact with the liquid at the monolayer interface, while the bromination of these interfaces indicates the number of unreacted vinyl groups that are accessible to the bromine.[81]

Contact Angle Titrations. We have previously demonstrated the utility of contact angle titrations for the characterization of acids and bases that are localized at a solid-water interface.[18,29] These titrations involve the measurement of the advancing contact angle, θ_a, as a function of the pH of the aqueous solution in contact with the monolayer. In determining contact angle titration curves for the monolayers studied here, the values of θ_a for every pH were measured on a single substrate. After measuring the contact angle for a solution of a given pH, the substrate was washed and dried prior to measurements utilizing a solution

of different pH. During this procedure the substrates became visibly contaminated, even when examining the low energy methyl- and vinyl-terminated monolayers. In order to minimize any systematic error resulting from this contamination, we measured the contact angles for pH = 1 - 11 at random. Because of the instability of the silane monolayers in basic solution, the contact angles for pH 12 and 13 were measured last. The determination of each of these contact angles was rapid (< 3 min) and within this time we did not observe any destruction of the monolayer as a result of exposure to the basic drops.

Figure 15 presents the contact angle titrations for methyl-, vinyl-, hydroxyl-, carboxyl-, and methyl ester-terminated alkylsiloxane monolayers. Neither the methyl- nor vinyl-terminated monolayers exhibited a significant change in contact angle as a function of pH. The apparent drift for the vinyl-terminated monolayer is probably an artifact of using $\cos\theta$ to represent the energy of the surface: the full range of contact angles observed for this sample was only 4°. With the methyl ester-terminated monolayer we observed a small (5-11°) decrease in θ_a at high pH. A similar decrease (6°) was found for the hydroxyl-terminated monolayer generated by hydroboration of a vinyl-terminated monolayer. We attribute this decrease to contamination of the surface and, in the case of the methyl-ester, hydrolysis of the ester moiety since the contact angles at low pH for these two monolayers were reduced after the titrations had been

completed. The acid-terminated monolayer, which was prepared by oxidation of a vinyl-terminated monolayer with $KMnO_4/NaIO_4$, also exhibited a pH dependence in its contact angle. Unlike the alcohol- and ester-terminated monolayers, however, the contact angle at low pH for these acid surfaces was unaffected by exposure of the monolayer to the basic solutions.

We define the $pH_{1/2}$ of a surface-localized carboxylic acid as the pH at which the value of $\cos\theta_a$ is halfway between that of $\cos\theta_a$ at pH 1 and pH 13[29] and the pH at which ionization of the carboxylic acid first appears (as reflected in a decrease in θ) as pK_i. The latter is probably more interpretable.[82] We note that, because of charge localized at the surface of the monolayer, the pH in the aqueous layer next to the monolayer may not be the same as the pH of the bulk solution.[83]

The fact that $pK_i \geq 6$ establishes that, to attain the same degree of ionization, the interfacial $-CO_2H$ groups require significantly higher values of solution pH than do the $-CO_2H$ groups in soluble carboxylic acids.[84] This decrease in acidity, which is also observed for carboxylic acid interfaces on polyethylene, probably reflects the fact that the interfacial carboxyl groups were in an environment of low dielectric constant.[29]

Interfaces Including Mixtures of Methyl and Carboxylic Acid Groups. We have investigated the effect of dilution of the carboxylic acid in the monolayer on the

apparent acidity of that acid by creating interfaces that had

mixtures of terminal carboxylic acid and methyl groups. The

method for creating such interfaces had to be chosen

carefully. There is evidence from other systems that, when

the alkyl tails of the molecules used to create "mixed"

monolayers are of different size or have different

polarities, the composition of the monolayer may differ

markedly from that of the solution from which it is

formed.[9,10] Our method for preparing monolayers that

contained mixtures of terminal functionalities probably

minimized this problem. The monolayers studied here were

prepared from solutions containing both HTS

($Cl_3Si(CH_2)_{15}CH=CH_2$) and $Cl_3Si(CH_2)_{15}CH_3$. Since the two

silanes are similar in structure, polarity, and size, we

believe that the ratio of vinyl and methyl groups in the

resulting monolayer closely mirrored that in the solution

from which they were prepared. Oxidation of the vinyl groups

in these monolayers by $KMnO_4$ and $NaIO_4$ yielded the mixed

methyl and acid monolayers of interest to us. We assume, in

the absence of any supporting data, that the yield on

conversion of vinyl to carboxylic acid groups was the same in

all of these samples. Since the oxidation removed one carbon

atom from the vinyl group, the numbers of carbon atoms (16)

in the methyl- and acid-terminated molecules were the same.

Figure 16 presents contact angle titrations for

carboxylic acid-containing monolayers prepared by oxidation

of monolayers that incorporated HTS in fractions from 0 to

100%. The fraction of carboxylic acids in these monolayers was probably ~ 80% that of the olefinic component. We note three important features of these mixed systems. First, as the concentration of acid groups within the monolayer increased, the monolayers became more hydrophilic. The contact angles of water ($\theta_a^{H_2O}$ = 30 - 108°) appeared to mirror the presumed composition of the outer interface. Second, the values of pK_i and $pH_{1/2}$ became larger as the concentration of the hydrophobic methyl tail group increased.[85] Third, the shape of the titration curve for 100% (and perhaps also for 80%) $-CO_2H$ groups probably contains a substantial element of artifact. The shapes of these curves almost certainly do not reflect solely a pH-dependent conversion of $-CO_2H$ to $-CO_2^-$ groups, but rather the intersection of such a curve (for pH $\leq$ 7.5) with the axis θ_a = 0° (for pH $\geq$ 7.5).[29,82] For a curve of this type, in which the value of $pH_{1/2}$ does not correspond in any simple way to the extent of ionization of the $-CO_2H$ groups, we cannot directly relate $pH_{1/2}$ to $pK_{1/2}$. The apparent decrease in the acidity of the carboxyl groups in the monolayer as the fraction of methyl groups increased probably results from the placement of the acid moiety in an increasingly hydrophobic environment.

Discussion

With the possible exception of CH_3SiCl_3, n-alkyl-trichlorosilanes form stable, well-ordered alkylsiloxane monolayers on silicon-silicon dioxide substrates. Our

results are in at least qualitative agreement with those of Sagiv[1-3,26-28] and others.[44] They also support our previous inference that wettability is a very surface-sensitive phenomenon.[86] Although covalent Si-O-Si linkages are clearly important in providing the exceptional stability of these monolayers, the degree that water is required to form these bonds is undefined. Ulman has used solutions of alkyl-trichlorosilanes in a hydrocarbon/CCl_4 solvent to form this type of monolayer.[44] The solvent for these preparations had been equilibrated with water prior to use. This procedure resulted in methyl-terminated monolayers that had up to 20 Å of contaminating material on the surface. Our procedure, using an anhydrous solution under a dry atmosphere, appears to lead to cleaner monolayers.[87] When cleaning procedures similar to those used by Ulman (wiping the surface with a cotton swab that had been dipped in ethanol) were applied to the monolayers prepared using our process, the length of the monolayer, as monitored by ellipsometry, decreased by no more than 1 Å. We have also used immersion times of up to 3 days to prepare monolayers from HTS without any loss of oleophobicity.

The ellipsometric measurements imply that the alkylsiloxane monolayers are fairly well-packed systems. X-ray reflectivity measurements indicate that these monolayers have a density slightly less than that of crystalline hydrocarbons, but higher than the density of liquid hydrocarbons.[47,48] Infrared spectroscopy also

supports the idea that these monolayers are well-ordered. The estimated angle of tilt for monolayers prepared from OTS $(CH_3(CH_2)_{17}SiCl_3)$, $14 \pm 18°$,[1,44] is only consistent with structures whose order approaches that of the crystalline state. These monolayers are therefore probably best described as liquid-crystalline or quasi-crystalline materials.

A limited study of reactions on terminal vinyl groups that were incorporated into alkylsiloxane monolayers indicated that synthetically useful transformations occurred readily, but that the yields were not quantitative. The bromination of the residual vinyl groups in $-CO_2H$ and $-CH_2OH$-terminated monolayers implied that more vinyl groups remained in the former than in the latter.

Acknowledgments

Experimental Section

General. Chemicals: Methyl-, ethyl, propyl-, hexyl-, 5-hexenyl-,heptyl-, octyl-, nonyl-, decyl-, undecyl-, dodecyl-, tetradecyl-, hexadecyl-, and octadecyltrichloro- silane were obtained from Petrarch and distilled prior to use. Silicon tetrachloride (Alfa, ultrapure), trichloro- silane (Petrarch), 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10- heptadecafluorodecyltrichlorosilane ($Cl_3Si(CH_2)_2(CF_2)_7CF_3$, Petrarch), undecenyl bromide (Pfaltz and Bauer), dihydrogen- hexachloroplatinate (Alfa), trifluoroacetic anhydride (Aldrich), and 1,6-dibromohexane (Aldrich) were used as received. Tetrahydrofuran and ether were dried by distillation from sodium/benzophenone. Hexane was distilled from Na/K alloy. Materials for preparation of monolayers: Silicon substrates were standard semiconductor grade silicon wafers (3 in. diameter) from Semiconductor Processing Corp. (Boston, MA) (n-type, laser grade) and Monsanto (p-type). Hydrogen peroxide (Mallinckrodt, 30%), and conc. sulfuric acid (Baker) were used as received. Hexadecane (Aldrich) and bicyclohexyl (Aldrich) were purified by percolation twice through neutral, grade 1, alumina (Fisher). Solvents purified in this manner passed the Bigelow test.[23] Carbon tetrachloride was dried by distillation from P_2O_5. Methylene chloride was dried by distillation from CaH_2. All solvents for preparation of the monolayers were stored under nitrogen. Materials for surface reactions: potassium permanganate ($KMnO_4$, Mallinckrodt), sodium meta-periodate

(NaIO$_4$, Mallinckrodt), K$_2$CO$_3$ (Mallinckrodt), NaHSO$_3$ (Fisher), BH$_3$-THF (Aldrich, 1 M), and bromine (Baker) were used as received.

Water was passed through an ion exchanger (Cole-Parmer) and distilled in a Corning Model AG-1b glass distillation apparatus. The buffers used for the contact angle titrations were as follows (0.05 M except where stated):[29] pH 1, 0.1 N HCl; pH 2, sodium phosphate; pH 3, malonic acid; pH 4, sodium phosphate; pH 5, acetic acid; pH 6, sodium phosphate; pH 7, sodium phosphate; pH 8, sodium phosphate; pH 9, boric acid; pH 10, boric acid; pH 11, sodium phosphate; pH 12, sodium phosphate; pH 13, 0.1 N NaOH.

The purities of reagents and adsorbates were checked by gas chromatography (Perkin-Elmer 3920B) and ^{1}H and ^{13}C NMR spectroscopy (using Bruker AM-250 and AM-300 spectrometers).

Preparation of Silicon Substrates. The silicon wafers (0.015 - 0.2 in. thick) were cut into strips 4 cm x 1.5 cm. These strips were placed in glass weighing bottles and covered with a solution of conc. H$_2$SO$_4$ and 30% H$_2$O$_2$ (70:30 v/v).[88] (Caution: 'piranha' solution reacts violently with many organic materials and should be handled with care.) After the mixture had been heated for 30 min at 90 °C, it was cooled to room temperature and the liquid was poured off. The silicon was immediately rinsed by first completely covering the substrates with distilled water and then decanting the liquid. This process was repeated a minimum of five times. The substrates were stored under water until

use. The silicon was used within two days of its cleaning. After longer times sufficient organic species had accumulated at the air-water interface to recontaminate the samples. Clean substrates were completely wetted by water.

Formation of Self-Assembled Monolayers. The cleaned silicon strips were removed from water using PTFE-coated forceps (Pelco). After all traces of water had been removed by exposing the sample to a stream of argon for 15 - 30 sec, the silicon was placed in a scintillation vial that had been thoroughly rinsed with distilled water and acetone and dried in an oven at 150 °C. These vials contained approximately 20 mL of an unstirred 0.1-0.5% (by weight) solution of the alkyltrichlorosilane in bicyclohexyl or hexadecane. (For $Cl_3Si(CH_2)_{10}CO_2CH_3$ and $Cl_3Si(CH_2)_2(CF_2)_7CF_3$ 0.001% and 0.4% solutions in CCl_4 were used.) The containers were kept under a dry nitrogen atmosphere or in a desiccator containing P_2O_5 (Baker, "granusic"). After 1 - 48 h the substrate was removed from the deposition solution and rinsed in 20 mL of CH_2Cl_2. After this wash, the substrates were removed from the dry atmosphere and rinsed in 20 mL of $CHCl_3$ and then 20 mL of ethanol to remove any residual organic contaminants. The sample was then rinsed with ethanol dispensed from a 2-mL disposable pipette. The monolayer was dried under a stream of argon and contact angle and ellipsometric measurements were made immediately.

Contact Angle Measurements. Contact angles were determined on sessile drops using a Ramé-Hart Model 100 contact angle goniometer equipped with a controlled environment chamber. The relative humidity in the chamber was maintained at greater than 80% by filling the wells of the chamber with water. The temperature was not controlled and varied from 20 - 25 °C. The volume of the drop used was 3 µL; the observed contact angle was, however, independent of the volume of the drop over the range of 1 to 20 µL. The sessile drops were applied to the surface by first forming a 2-µL drop at the tip of a 50-mL syringe (Scientific Glass Engineering, Austin, Tx) that was equipped with a PTFE-coated needle and a repeating dispenser (Hamilton). The syringe was lowered to the the surface by turning the screw upon which the syringe platform rested. After the drop had come in contact with the monolayer, the needle was removed by rotating the screw in the opposite direction. While the needle was raised, another µL of solvent was added to the drop. Contact angles were determined within 1 minute of applying the drops to the monolayer. The tangent to the drop at its intersection with the surface was estimated visually. All reported values are the average of at least 6 measurements taken on both sides of at least three drops. Values obtained in this manner were typically 2 to 3° less than those from the maximum advancing angle technique described by Troughton et. al.[18]

Ellipsometry Measurements. Ellipsometry
measurements were made with a Rudolph Research Model
43603-200E thin film ellipsometer. The light source was a
He-Ne laser ($\lambda = 6328$ Å). The angle of incidence was 70.0°
and the compensator was set at -45.0°. The measurements
necessary for the calculation of the film thickness consisted
of the determination of two sets of polarizer and analyzer
readings for the silicon substrate and of the corresponding
values for the substrate coated with a monolayer film.

Each set of analyzer and polarizer angles, measured in
zones 1 and 3,[46] was the average of at least four
measurements taken at different locations (separated by at
least 1 cm) on the sample. The angles that comprised this
average had a maximum scatter of $\pm$ 0.15°. These measurements
were determined in air for the bare substrate within 3 min of
its removal from water. The substrate was placed in solution
immediately after these measurements. The ellipsometric
angles for the substrate-monolayer systems were measured no
more than 5 min after the samples had been washed with
ethanol.

The refractive index of each substrate was determined
directly from the analyzer and polarizer readings for the
uncoated silicon. Refractive indices for the various
substrates ranged from 3.84-3.88. This index reflects the
combined contributions from the surface silica and the
underlying bulk silicon. Using literature values for the
refractive indices of silicon and silicon dioxide,[89] we have

estimated that the oxide layer was 10 to 20 Å in thickness.[90] This thickness is consistent with those derived from scanning tunnelling electron microscopy,[36] high resolution electron microscopy,[91] and other ellipsometric studies.[92]

The thicknesses of the monolayers were calculated using the algorithm of McCrackin.[46] For this calculation we assumed that the monolayer had a refractive index of 1.45 and was completely transparent to the laser beam. This index is approximately that of both liquid and solid straight-chain hydrocarbons (n = 1.42-1.44).[93] Altering this value by 0.05 resulted in less than a 1 Å change in the calculated thickness of the monolayer. The algorithm yielded two values for the length of the monolayer, both of which were complex. Since the length of the monolayer must be real, we chose the real part of the complex number with the smaller imaginary component as the thickness of the monolayer. The other choice was inherently unreasonable since it was greater than 1000 Å. Thicknesses determined in this fashion are accurate to ± 2 Å.

X-ray Photoelectron Spectroscopy. The XPS spectra were obtained using a Surface Science Laboratories Model SSX-100 spectrometer (monochromatized Al Kα X-ray source; 10^{-8} - 10^{-9} torr) referenced to Au 4f7/2 at 84.0[94] according to ASTM STP 699. Samples were washed with ethanol and introduced into the spectrometer. A survey spectrum (resolution 1.1 eV, spot size 1000 μ, 1 scan) and high resolution spectra of the C 1s, O 1s, and Si 2p regions

(resolution 0.16 eV, spot size 300 μ, 5 - 30 scans) were taken for each sample. High resolution spectra were also obtained for F 1s and Br 3d when these elements were present in the monolayer. Atomic compositions were determined using standard multiplex fitting routines with the following sensitivity factors: C 1s, 1.00; Si 2p, 0.902; O 1s, 2.49; Br 3d, 3.188; F 1s, 3.33.[72]

16-Heptadecenyl Bromide. This compound was prepared using the procedure of Friedman and Shani.[95] Undecenyl bromide (20.0 g, 86 mmol) and magnesium (3.3 g, 136 mg-atom) were sealed in a dry heavy-walled glass bottle. The bottle was evacuated and the atmosphere was replaced with argon. Dry, degassed THF (50 mL) was added via cannula and the bottle was placed in an ultrasonic bath for 24 h. The resulting solution of Grignard reagent was added slowly to a cooled, degassed solution containing 1,6-dibromohexane (21.0 g, 86 mmol), and Li_2CuCl_4 (10 mL of a 0.1 M THF solution, 1 mmol) in THF (55 mL). The solution was stirred for 2 h at 5 °C, after which the reaction was quenched with 200 mL of saturated aqueous ammonium chloride solution. Stirring overnight extracted the copper salts into the aqueous layer. The aqueous layer was extracted with ether (3 x 100 mL) and the combined organic layers were then extracted with saturated aqueous sodium chloride (2 x 100 mL). After the solution had been dried over magnesium sulfate, the solvent was evaporated and the remaining oil was dried under vacuum. The crude product was

eluted in 3-g batches with hexane through a silica column (radius-2.5 cm, length-31 cm). All fractions containing the desired bromide, still impure, were collected. This process was continued until the material had been eluted three times. The enriched bromide was then purified in 2.2 g batches by MPLC through a Lobar© (E. M. Merck) prepacked column (radius-3.7 cm, length-44 cm) containing silica-60 (63-125 μ) using hexane as the eluent. The solvent was delivered by a FMI RP-SY pump at a flow rate of 6 mL/min and fractions were collected every 1.5 min. The fractions containing the pure bromide were combined and the solvent was evaporated. The isolated yield was 8.1 g (25 mmol, 30%). ^{1}H NMR (CDCl3): δ 5.8 (m, 1), 4.9 (m, 2), 2.0 (m, 2), 1.8 (m, 2), 1.5-1.1 (m, 24). ^{13}C NMR (CDCl3): δ 139.0, 114.0, 33.85, 33.73, 32.94, 29.72, 29.67, 29.57, 29.49, 29.21, 29.04, 28.86, 28.27. Mass spectrum, m/z (relative intensity): 318 (2), 316 (2), 164 (6), 162(6), 41 (100). Anal. Calcd. for $C_{17}H_{33}Br$: C, 64.32; H, 10.50; Br, 25.17. Found: C, 64.51; H, 10.60; Br, 25.3.

16-Heptadecenyltrichlorosilane. This compound was prepared using the procedure of Whitemore, et. al.[34] Magnesium (2.02 g, 83 mg-atom), 16-heptadecenyl bromide (5.00 g, 16 mmol), and dry THF (75 mL) were placed in a dry heavy-walled glass bottle. The container was then sealed with a septum and metal cap. After the bottle had been cooled to -78 °C, the atmosphere was replaced by evacuating and purging with argon (3 cycles). The bottle was then

warmed to room temperature and placed in an ultrasonic bath
(10 h). A 500-mL round-bottomed flask with a sidearm was
equipped with a magnetic stirring bar and flame dried.
Silicon tetrachloride (4.0 mL, 35 mmol) and dry ether (50 mL)
were added to the flask while continually purging it with
argon. A water-cooled condenser was attached to the flask
which was then sealed with a septum. The solution was
degassed using a procedure identical to that for the Grignard
reagent. The flask was warmed to room temperature and the
Grignard solution was added through a cannula. The solution
was heated at reflux (12 h) and then cooled to room
temperature. The condenser was removed and a liquid
nitrogen-cooled trap was connected. The solvent and residual
tetrachlorosilane were removed by a trap-to-trap
distillation. The remaining solid was triturated with dry
hexane (2 x 125 mL). This solution was transferred via
cannula through a sintered glass filter to a dry 500-mL
round-bottomed flask. A cold trap was attached and the
hexane was removed under vacuum After the remaining solid
had been warmed to form an oil, the liquid was transferred by
pipette to a dry Kugelrohr distillation apparatus. The crude
product was distilled and a fraction was collected from
91 °C (0.003 torr) to 119 °C (0.008 torr). This material was
then redistilled in a short path distillation apparatus. The
product was collected as the fraction that boiled between
105 °C (0.005 torr) and 115 °C (0.005 torr). The product
(2.87 g, 49%) was isolated as a clear oil. ^{1}H NMR (CDCl$_3$):

δ 5.8 (m, 1), 4.9 (m, 2), 2.0 (m, 2), 1.7-1.1 (m, 28).
^{13}C NMR (CDCl$_3$): δ 139.2, 114.1, 33.8, 31.6, 29.66, 29.60,
29.52, 29.37, 29.17, 29.01, 24.4, 22.3. Anal. Calcd. for
C$_{17}$H$_{33}$Cl$_3$Si: C, 54.89; H, 8.96; Cl, 28.59. Found: C, 55.73;
H, 9.17; Cl, 27.46.

By both NMR spectroscopy and elemental analysis this
material contained an approximately 3% impurity of 1-hepta-
decene. The presence of this compound has no effect on the
formation of monolayers from the trichlorosilane.

10-Undecenyltrichlorosilane. This compound was
prepared by a procedure similar to that for 16-hepta-
decenyltrichlorosilane. ^{1}H NMR (CDCl$_3$): δ 5.8 (m, 1), 5.0
(m, 2), 2.0 (m, 2), 1.7-1.2 (m, 16). ^{13}C NMR (CDCl$_3$):
δ 139.0, 114.1, 33.88, 31.89, 29.52, 29.39, 29.16, 29.09,
29.04, 24.47, 22.38. Anal. Calcd. for C$_{11}$H$_{21}$Cl$_3$Si: C, 45.91;
H, 7.37; Cl, 36.96. Found: C, 45.88; H, 7.36; Cl, 36.93.

Methyl 11-Trichlorosilylundecanoate. Methyl
10-undecenoate (12.0 g, 61 mmol), dihydrogenhexachloro-
platinate(II) (5.1 mL of a 0.01 M THF solution, 0.051 mmol),
and trichlorosilane (7.9 mL, 78 mmol) were placed under argon
in a dry heavy-walled glass tube (diameter-2.5 cm,
length-21 cm) that was equipped with a sidearm and a 0-10 mm
PTFE stopcock. The solution was degassed (freeze-pump-thaw,
3 cycles) and the tube was sealed under vacuum at -195 °C.
The tube was warmed to room temperature and heated in an oil
bath (98 °C, 37 h). It was then cooled to -195 °C and a
liquid nitrogen-cooled trap was attached. The reaction

solution was warmed to room temperature and the excess
trichlorosilane was removed by a trap-to-trap distillation.
The remaining liquid was transferred by pipette to a dry
Kugelrohr distillation apparatus and the residual THF was
removed under vacuum. The liquid was distilled and the
product was collected from 98 °C (0.03 torr) to 120 °C
(0.03 torr) (13.4 g, 40 mmol, 67%). ^{1}H NMR (CDCl$_3$): δ 3.7
(s, 3), 2.3 (t, 2), 1.8-1.1 (m, 18). ^{13}C NMR (CDCl$_3$):
δ 175.1, 50.6, 34.0, 31.7, 29.26, 29.18, 29.11, 29.06, 28.89,
24.9, 24.3, 22.2. Anal. Calcd. for C$_{12}$H$_{23}$Cl$_3$O$_2$Si: C, 43.18;
H, 6.96; Cl, 31.86. Found: C, 43.34; H, 7.01; Cl, 31.94.

Rate of Formation of Monolayers. Formation of the
monolayer film was monitored by ellipsometry and contact
angle measurements. The film was prepared by the procedures
described above. Measurements of contact angles (both water
and hexadecane) and thickness were made on a single substrate
which was immersed repeatedly in a solution of tetradecyl-
trichlorosilane (Cl$_3$Si(CH$_2$)$_{13}$CH$_3$) in bicyclohexyl (0.01 M).
The sample was removed from the adsorption solution and
washed with chloroform and ethanol. After determination of
the thickness by ellipsometry, the sample was washed with
ethanol and the aqueous contact angle was measured. The
ethanol wash was repeated before measurement of the contact
angle for hexadecane. The sample was then washed with
ethanol, dried under a stream of argon, and reimmersed in the
adsorption solution.

Stability of Monolayers. The stability of the monolayers was monitored by a procedure similar to that for following the kinetics of formation. For both 0.1 N HCl and 0.1 N NaOH the sample was repeatedly immersed in the solution for timed intervals. The monolayers were removed from the solution and washed with distilled water and ethanol. The thickness and the contact angles with water and hexadecane were measured as above. For the hexadecane desorption the solvent was kept in a glass vial in an oil bath at 75 °C. The monolayer was removed at timed intervals and washed with ethanol before the ellipsometry and contact angle measurements were taken.

Surface Reactions. Permanganate-Periodate Oxidation. Stock solutions of $KMnO_4$ (5 mM), $NaIO_4$ (195 mM), and K_2CO_3 (18 mM) in water were prepared. Immediately prior to the oxidation 1 mL from each of these solutions was combined with 7 mL of distilled water to create the oxidizing solution ($KMnO_4$, 0.5 mM; $NaIO_4$, 19.5 mM; K_2CO_3, 1.8 mM, pH 7.5). The vinyl- and methyl-terminated monolayers were placed in this solution for periods of 24 h. (The kinetics of this reaction were monitored on a single sample by an identical procedure over shorter intervals.) The samples were removed from the oxidant and rinsed in 20 mL of each of $NaHSO_3$ (0.3 M), water, 0.1 N HCl, water, and ethanol.

Hydroboration. The vinyl-terminated monolayers were placed in a glass vial which was then sealed with a rubber septum. The atmosphere was purged by passing argon gas

through the container for 30 min. All solvent transfers were performed through cannula. Sufficient BH$_3$-THF complex (1 M) to completely cover the silicon (ca. 20 mL) was added. After 2 h the borane solution was removed and dry THF was added. The THF was removed and approximately 15 mL of 30% H$_2$O$_2$/0.1 N NaOH was transferred into the vial. After 3 min the vial was opened to the atmosphere. The monolayer was then rinsed thoroughly with water and ethanol.

Trifluoroacetylation of Hydroxyl-terminated Monolayers. The hydroxyl-terminated monolayers generated by hydroboration were placed in a 2% (v:v) solution of trifluoroacetic anhydride in hexane. After 2 min the substrate was removed from solution and rinsed with ethanol dispensed from a pipette. The aqueous contact angles of these surfaces were stable during the time necessary to measure these angles.

Bromination. The vinyl monolayers were placed for 2 h in a 2% (by volume) solution of elemental bromine in CH$_2$Cl$_2$. The wafers were then rinsed with CH$_2$Cl$_2$ (2 x 20 mL) and ethanol.

Mixed Acid and Methyl Surfaces. Stock solutions of hexadecyltrichlorosilane and 16-heptadecenyltrichlorosilane in hexadecane (25 mM) were prepared. These were then mixed in the appropriate ratios to generate solutions (25 mM total silane concentration) containing 0, 20, 40, 60, 80, and 100% of the vinyl-terminated silane. Monolayers were prepared from these solutions according to the methods described

above.   Oxidation of the vinyl groups with $KMnO_4/NaIO_4$ using

the procedure described above yielded monolayers tnat

contained terminal methyl and carboxyl groups.

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and refractive index of a thin film. This simultaneous
determination relies on the precision of the measurement of
the analyzer and polarizer angles. Our accuracy is such
that, for films less than 100 Å in thickness, we cannot
obtain values for both the length and the refractive index of
the alkylsiloxane monolayers. See reference 46.

51. Infrared spectroscopy using polarized radiation suggests
that these monolayers are oriented nearly perpendicular to
the surface (tilt angle, ϕ, = 14 $\pm$ 18°). This orientation
would lower the lengths of alkylsiloxane monolayers by 3%
compared to alignment with the normal to the plane of the
monolayer. For a monolayer prepared from OTS the change in
length for ϕ = 14° compared to ϕ = 0° would be 0.8 Å. See
references 1 and 44.

52. All distances are derived from standard bond lengths
assuming that all bond angles in the <u>trans</u> chain are 109.5°.

53. The contribution of the methyl group is estimated by
summing the covalent radii of carbon (0.77 Å) and hydrogen
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71. We have continued to use an index of refraction of 1.45 for alkylsiloxane monolayers even after modification of the terminal vinyl group. This approach is clearly arbitrary but, even for the bromination reactions discussed below, using the refractive index of elemental bromine (1.66) alters our estimate of the change in thickness by only ~ 0.4 Å.

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74. The carbon atom of a carboxyl group is expected to have a shift of 4.5 eV relative to the carbon atom of a methylene group. See reference 57.

75. The asymmetry of the methylene signal could be modelled by an additional peak at + 1.5 eV relative to the $-CH_2-$ signal. The energy observed here is 1.2 eV higher than that reported in the literature (ref. 57) for a carbon atom alpha to a carboxylic acid. The intensity of this peak was equal to that of the carbon atom in the acid group.

76. Although the range of contact angles (θ_a^{H2O} = 25-38°) was larger than that of the initial vinyl-terminated interfaces, in terms of surface free energy this range corresponds to only ~ 15% of the total change induced by the oxidation. This range was calculated by comparing the difference in $\cos\theta_a$ for the maximum and minimum contact angles of the acid-terminated monolayers to the difference in $\cos\theta_a$ between the vinyl-terminated and the (average) acid-terminated monolayers.

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monolayers were partially disordered. Some angle-resolved XPS spectra indicated that the location of -OH and -CHBrCH$_2$Br groups in vinyl-terminated monolayers that had undergone hydroboration or addition of bromine was at or near the air-monolayer interface. Such spectra were not, however, reproducible.

80. Bain, C. D., unpublished results.

81. The accessibility of bromine to unreacted vinyl groups in these two types of oxidized monolayers may be different. The KMnO$_4$/NaIO$_4$ oxidation, which does not increase the length of the monolayer, presumably leaves the unreacted vinyl groups at the air-monolayer interface. The hydroboration adds a monolayer of hydroxyl groups over the unreacted vinyl groups. The stoichiometry and products of reaction may also be different (for example, the extent of formation of bromoethers or bromolactones may differ).

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90. These estimates are crude. Ellipsometry actually yields a complex value for the thickness of the monolayer. For well-behaved systems, such as the monolayers described here, more than 95% of the absolute value of the length is real. For the estimates of the oxide thickness the length was more than 60% imaginary. This result suggests that the silicon oxide on the substrate did not have a refractive index equal to the literature value. The ellipsometric measurements reported here relied on the direct determination of an "effective" index of refraction for the substrate, which included the contributions from the bulk silicon and the surface oxide of the substrate. The lack of a definitive index of refraction for the individual Si and SiO_2 layers of the substrate should, therefore, have had little effect on the measured thicknesses of the monolayers. A demonstration of the validity of the use of an effective refractive index for the substrate is found in reference 45, pp 332-340.

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Captions

Figure 1. Schematic representation of the formation of alkylsiloxane monolayers by adsorption of alkyltrichlorosilanes $(R(CH_2)_nSiCl_3, n = 0 - 17)$ from solution onto silicon-silicon dioxide (Si/SiO_2) substrates. The SiO_2 layer was 10 - 20 Å in thickness. The monolayers were 6 - 27 Å in thickness. The text discusses the bonding between the substrate and the monolayer.

Figure 2. Methyl-terminated alkylsiloxane monolayers prepared by adsorption of n-alkyltrichlorosilanes, $CH_3(CH_2)_nSiCl_3$, onto Si/SiO_2 substrates. Each datum represents measurements on a different silicon substrate. Usually monolayers containing a given chain length were prepared in at least two independently constituted solutions of the alkyl-trichlorosilane. (A) Advancing contact angles, θ_a. The contact angles of water are above the dashed line; those of hexadecane are below. (B) Ellipsometric thicknesses (Å). The solid line represents the best linear least-squares fit for $n = 1 - 17$.

Figure 3. XPS spectra of alkyltrichlorosilane monolayers, $R(CH_2)_9SiCl_3$ ($R = CH_3CH_2-$, $CH_2=CH-$, CH_3OCOCH_2-), on Si/SiO_2 substrates: survey spectra (left) and high resolution spectra of the carbon 1s (center) and silicon 2p (right) regions. The C 1s and Si 2p spectra are each normalized to the same maximum peak height.

Figure 4. Angle-dependent XPS survey spectra of a monolayer prepared by adsorption of octadecyltrichlorosilane ($CH_3(CH_2)_{17}SiCl_3$, OTS) onto an Si/SiO_2 substrate. Spectra were obtained at take-off angles of 90°, 35°, and 15°.

Figure 5. Models for the binding of alkylsiloxane monolayers to Si/SiO_2 substrates. (A) The silicon atom in the alkyltrichlorosilane, $RSiCl_3$, forms three bonds to hydroxyl groups at the surface of the substrate oxide layer. The formation of this structure does not require any adsorbed water. (B) The silicon atom in $RSiCl_3$ forms one or two bonds to surface hydroxyl groups. The remainder of the the Si-Cl bonds are hydrolyzed, resulting in the formation of silanols (-SiOH) and Si-O-Si linkages between adjacent alkylsilanes. The Si-O-Si links can also bind within the monolayer alkylsilanes whose silicon atom has not formed any bonds to the surface.

Figure 6. Ratio of the atomic intensities of the carbon 1s (C) and silicon substrate 2p (Sub) peaks in XPS for alkylsiloxane monolayers prepared from $CH_3(CH_2)_nSiCl_3$. The intensity of the substrate is a mathematical construct from the intensities of the Si 2p, SiO_2 2p, and O 1s signals (see appendix in supplemental material). The parameter C_∞/Sub_∞ is the ratio of the volume atomic densities of crystalline silicon and of carbon within crystalline hydrocarbons. This parameter, C_∞/Sub_∞, is theoretically 0.8. The function $\ln(C/Sub - C_\infty/Sub_\infty)$ is approximately linear for $C_\infty/Sub_\infty = 0.6 - 1.5$.

Figure 7. Rate of formation of an alkylsiloxane monolayer prepared from $CH_3(CH_2)_{13}SiCl_3$ (TTS, 0.01 M) at 20 °C and 30% relative humidity. (A) Advancing contact angles of water and hexadecane. (B) Ellipsometric thicknesses. The calculated thickness for this monolayer, $L_{calculated} = 21.1$ Å, is based on the assumption of a _trans_-extended conformation for the alkyl groups, with the chain axis perpendicular to the surface.

Figure 8. Stability of alkylsiloxane monolayers prepared from $CH_3(CH_2)_{13}SiCl_3$ (TTS) and exposed to 0.1 N HCl at 20 °C ($\bigcirc$), 0.1 N NaOH at 20 °C ($\blacksquare$), or hexadecane ($\bullet$) at 75 °C. (A) Advancing contact angles. The contact angles of water are above the dashed line; those of hexadecane are below. (B) Ellipsometric thicknesses. The negative thickness after exposure to the 0.1 N NaOH probably indicates etching of the surface oxide after the monolayer had been removed.

Figure 9. Vinyl-terminated alkylsiloxane monolayers prepared by adsorption of $CH_2=CH(CH_2)_nSiCl_3$ (n = 4,9,15) onto Si/SiO_2 substrates. Each datum represents measurements on a different silicon substrate. (A) Advancing contact angles. The contact angles of water are above the dashed line; those of hexadecane are below. (B) Ellipsometric thicknesses (Å). The solid line represents the best linear least squares fit. The increment in thickness per methylene group is 1.44 Å.

Figure 10. Oxidation of methyl- and vinyl-terminated alkylsiloxane monolayers prepared from $CH_3(CH_2)_{13}SiCl_3$ ($\bigcirc$) and $CH_2{=}CH(CH_2)_{15}SiCl_3$ ($\bullet$) by $KMnO_4$ (0.5 mM) / $NaIO_4$ (19.5 mM) at 20 °C. The advancing contact angles of water (A) and ellipsometric thicknesses (B, in Å) were measured as a function of the time, T, of oxidation.

Figure 11. XPS spectra (survey and high resolution of the carbon 1s region) of reaction products from vinyl-terminated alkylsiloxane monolayers prepared from $CH_2{=}CH(CH_2)_nSiCl_3$ (n = 4, 9, 15): carboxylic acid from oxidation with $KMnO_4/NaIO_4$, alcohol from hydroboration (1. BH_3 2. $H_2O_2/NaOH$), and 1,2-dibromide (and related brominated species) from reaction with elemental bromine (Br_2). The C 1s spectra are normalized to the same maximum peak height. As n increases, the signal from the functionalized carbon atom(s) decreases relative to the signal from the methylene groups in the monolayer.

Figure 12. Reaction products from vinyl-terminated alkylsiloxane monolayers prepared from $CH_2=CH(CH_2)_nSiCl_3$ (n = 4, 9, 15): carboxylic acid from oxidation with $KMnO_4/NaIO_4$ (O), alcohol from hydroboration (1. BH_3 2. $H_2O_2/NaOH$) (■), and 1,2-dibromide (and related brominated species) from reaction with elemental bromine (Br_2) (●). Each data point represents measurements on a different substrate. The markers represent typical errors in the measurements of contact angles and ellipsometric thicknesses. (A) Advancing contact angle of water. (B) Change in ellipsometric thickness (product minus reactant) of the monolayer as a result of the surface reaction.

Figure 13. XPS spectra of alkylsiloxane monolayers prepared from $CH_2=CH(CH_2)_9SiCl_3$ and treated with trifluoroacetic anhydride (2% v:v in hexanes): survey (left) and high resolution of the carbon 1s region (right). The C 1s spectra are normalized to the same maximum peak height. (A) Vinyl-terminated monolayer. (B) Alcohol-terminated monolayer prepared from A by hydroboration (1. BH_3 2. $H_2O_2/NaOH$).

Figure 14. Extent of reaction within alkylsiloxane
monolayers: XPS spectra [survey (left), high
resolution of the carbon 1s (center) and bromine
3d regions (right)] of vinyl-, hydroxyl-, and
carboxylic acid-terminated monolayers prepared
from $CH_2=CH(CH_2)_{15}SiCl_3$ (HTS) and then
functionalized with elemental bromine (Br_2, 1%
in CH_2Cl_2). The C 1s and Br 3d spectra are each
normalized to the same maximum peak height. The
Br 3d spectra for B and C have been smoothed
using a nine-point algorithm with a symmetrical
triangle convolution function (Savitsky, A.;
Golay, M. J. E. Anal. Chem. **1964**, <u>36</u>, 1627-
1639). The dashed lines in the Br 3d spectra
for B and C represent the amount of bromine
remaining on these surfaces relative to A.

(A) "-CHBrCH$_2$Br"-terminated monolayer prepared
by bromination of the vinyl-terminated monolayer
prepared from HTS. (B) Bromination product of
the acid-terminated monolayer prepared by
oxidation with $KMnO_4/NaIO_4$ of a monolayer
prepared from HTS. This monolayer contained
both -CO$_2$H and and "-CHBrCH$_2$Br" groups.

(C) Bromination product of the alcohol-
terminated monolayer prepared by hydroboration
(1. BH$_3$ 2. H$_2$O$_2$/NaOH) of a monolayer prepared
from HTS. This monolayer contained both -CH$_2$OH

and "-CHBrCH$_2$Br" groups. For A, B, and C "-CHBrCH$_2$Br" represents the 1,2-dibromide and related brominated species.

Figure 15. Dependence of the advancing contact angle of water, θ_a, on pH for alkylsiloxane monolayers: methyl-terminated monolayer prepared from CH$_3$(CH$_2$)$_{13}$SiCl$_3$ (■), vinyl-terminated monolayer prepared from CH$_2$=CH(CH$_2$)$_{15}$SiCl$_3$ (HTS) (□), methyl ester-terminated monolayer prepared from CH$_3$OCO(CH$_2$)$_{10}$SiCl$_3$ (▲), alcohol-terminated monolayer prepared by hydroboration of a monolayer prepared from HTS (○), and acid-terminated monolayer prepared by oxidation (KMnO$_4$/NaIO$_4$) of a monolayer prepared from HTS (●).

Figure 16. Dependence of the advancing contact angle of

water, θ_a, on pH for alkylsiloxane monolayers

that contained mixtures of terminal $-CH_3$ and

$-CO_2H$ groups. Monolayers were prepared by

adsorption from solutions that contained

$CH_2=CH(CH_2)_{15}SiCl_3$ and $CH_3(CH_2)_{15}SiCl_3$. The

percentages of the vinyl-terminated alkylsilane

in these solutions were 0, 20, 40, 60, 80, and

100%. The vinyl groups in these monolayers were

then oxidized to carboxylic acid moieties using

$KMnO_4/NaIO_4$. Based on the studies summarized in

Figure 14, the yield of these oxidations was

probably ~ 80%. The solid vertical lines

represent values of $pH_{1/2}$. The dashed vertical

lines represent values of pK_i.

Scheme I. Methods for the syntheses of

alkyltrichlorosilanes.

The Structure and Reactivity of Alkylsiloxane Monolayers Formed by Reaction of Alkyltrichlorosilanes on Silicon Substrates

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Supplementary Material: Variation in Ellipsometric Angles.

Appendix

Variation in Ellipsometric Angles. We observed some spot-to-spot variation when measuring the analyzer and polarizer angles for each substrate. Since the use of ellipsometry requires a comparison of the uncoated substrate with the substrate-monolayer system, we attempted to measure the optical constants in the same spots on the bare substrate and the monolayer. We could not, however, achieve an absolute congruence. In Figure 1 we show the range, R, in polarizer values for the substrate plotted against those for the monolayer prepared on that substrate. These values have been converted from the measured angles to the equivalent length in angstroms. In general the observed range was less than 1 Å and rarely exceeded 2 Å. The data are clustered randomly about the line $R_{substrate} = R_{monolayer}$. This graph suggests that the observed variation in the polarizer angles was probably the result of variations in the structure of the substrate, rather than inhomogeneities in a contaminating layer.

Appendix

Escape Depth of an Electron. The intensity of a
given element, I, in the XPS measurement is the number of
electrons of a given energy that are detected by the
spectrometer. This measured intensity is lower than the
total number of electrons generated by photoionization
because of inelastic electron-electron collisions.[1] The
attenuation of the intensity is represented by an inelastic
loss factor, $e^{-d/\lambda}$ where λ is the escape depth (attenuation
length) of the electron and d is the distance that an
electron travels through the sample before emerging into the
vacuum. The alkylsiloxane monolayers are part of a three-
layer system: hydrocarbon, silicon dioxide, and silicon.
Since the attenuation length is a function of the energy of
the electron[2] and since the energies of the electrons that
are emitted from carbon, silicon, and oxygen are different,
the complete description of the passage of an electron
through an alkylsiloxane monolayer on a silicon-silicon
dioxide substrate requires a rather complicated analysis.

We have instead chosen to approximate the substrate as
an infinite layer of silicon. The intensity of the XPS
signal from this layer, I(sub), is a function of the
intensities of the silicon, I(Si), silicon dioxide, I(SiO_2),
and oxygen, I(O), signals. The specific form of I(sub) which
we shall use is given in equation A. This function

$$I(sub) = I(Si) + I(SiO_2) + 0.5\ I(O) \qquad (A)$$

represents an approximation which is valid for considerations of both mass and electron density within the substrate. The intensities that we shall use are the atomic intensities. These are related to the number of counts, N, by the photoionization cross-section, σ [3] (eq B). We shall assume that the intensity of the signal from the silicon substrate,

$$I = N\sigma^{-1} \qquad\qquad (B)$$

$$I(sub) = I_\infty(sub)e^{-x/\lambda} \qquad\qquad (C)$$

$$I(C) = I_\infty(C)[1 - e^{-x/\lambda}] \qquad\qquad (D)$$

I(sub), is given by equation C. Here I_∞(sub) is the intensity of an infinite silicon substrate and x is the distance an electron travels from the surface of the silicon through the monolayer. Similarly, the intensity of the peak from the carbon atoms in the monolayer can be viewed as the difference in intensities of two infinite carbon layers, one of which is displaced by a distance x (eq D). By using the same λ for both carbon and the silicon substrate, we have assumed that, over the range of electron energies used here (950 - 1400 eV), the escape depth is constant.

The distance x is related to the length of the monolayer and the takeoff angle of the detector. The takeoff angle for these measurements was 35°. We shall assume that the length of the monolayer is a function of the incremental chain

length per methylene group, 1.26 Å, and the number of carbon
atoms in the alkyl tail group, n.[4] Equation E shows the
relationship between x and n.

$$x = 1.26 \ n \ (\sin 35°)^{-1} \qquad \text{(E)}$$

The ratio between the carbon and silicon intensities is
given by equation F. Equation G, which is an alternative

$$\frac{I(C)}{I(Si)} = \frac{I_\infty(C)}{I_\infty(Si)} \ (e^{x/\lambda} - 1) \qquad \text{(F)}$$

$$\ln\left(\frac{I(C)}{I(Si)} + D\right) = \frac{x}{\lambda} + \ln D \qquad D = \frac{I_\infty(C)}{I_\infty(Si)} \qquad \text{(G)}$$

representation of equation F, is linear and has two
parameters, D and λ. We have used two methods for fitting
our data to equation G. The first assumes that, since we are
using atomic intensities, D is 0.80, the ratio of the atomic
densities (atoms per unit volume) of carbon in paraffins and
silicon. This one parameter approach gives an escape depth
of 26 Å.[5] The second technique treats both D and λ as
fitting parameters. Convergence of the two parameter model
yields D = 1.18 and λ = 38 Å. We have repeated these
calculations using an alternate form of I(sub), presented in
equation H. (The factor 30/14 represents the fraction that

$$I(sub) = I(Si) + (30/14) I(SiO_2) \qquad \text{(H)}$$

silicon contributes to the total number of electrons in SiO_2.) Calculations using this version of $I(sub)$ yield, for the one and two parameter approaches, escape depths of 29 Å and 47 Å (D = 1.49) respectively.

We note one further complication in this analysis. The intensity from the silicon atoms was reduced because of plasmon losses. A rather fortuitous result is that these losses should have no effect on the two-parameter model. In the one-parameter case, inclusion of the plasmon intensities would increase the escape depth, thus bringing the values for λ into closer agreement.

The number of approximations in this model precludes its use for a definitive determination of the attenuation length of an electron. The values obtained here are, however, in reasonable agreement with those derived from studies on other monolayer systems.[6,7]

References and Notes

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4. We ignore the difference in size between a methyl and a methylene group.

5. We have used only the data for chain lengths of 2 to 18 carbon atoms since the films prepared from CH_3SiCl_3 apparently were not monolayers.

6. Brundle, C. R.; Hopster, H.; Swalen, J. D. J. Chem. Phys. **1979**, 70, 5190-5196.

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Captions

Figure 1. Range in ellipsometric polarizer (P) angles for
alkylsiloxane monolayers on Si/SiO_2 substrates.
The range is the difference between the highest
and lowest measured values of P. The ranges are
presented in their angstrom equivalents
$(0.145° \approx 1 \text{ Å})$. Each data point represents the
range on the substrate (R_S) and the range on the
same substrate after formation of the monolayer
(R_m). The solid line is that expected if R_m
equals R_S
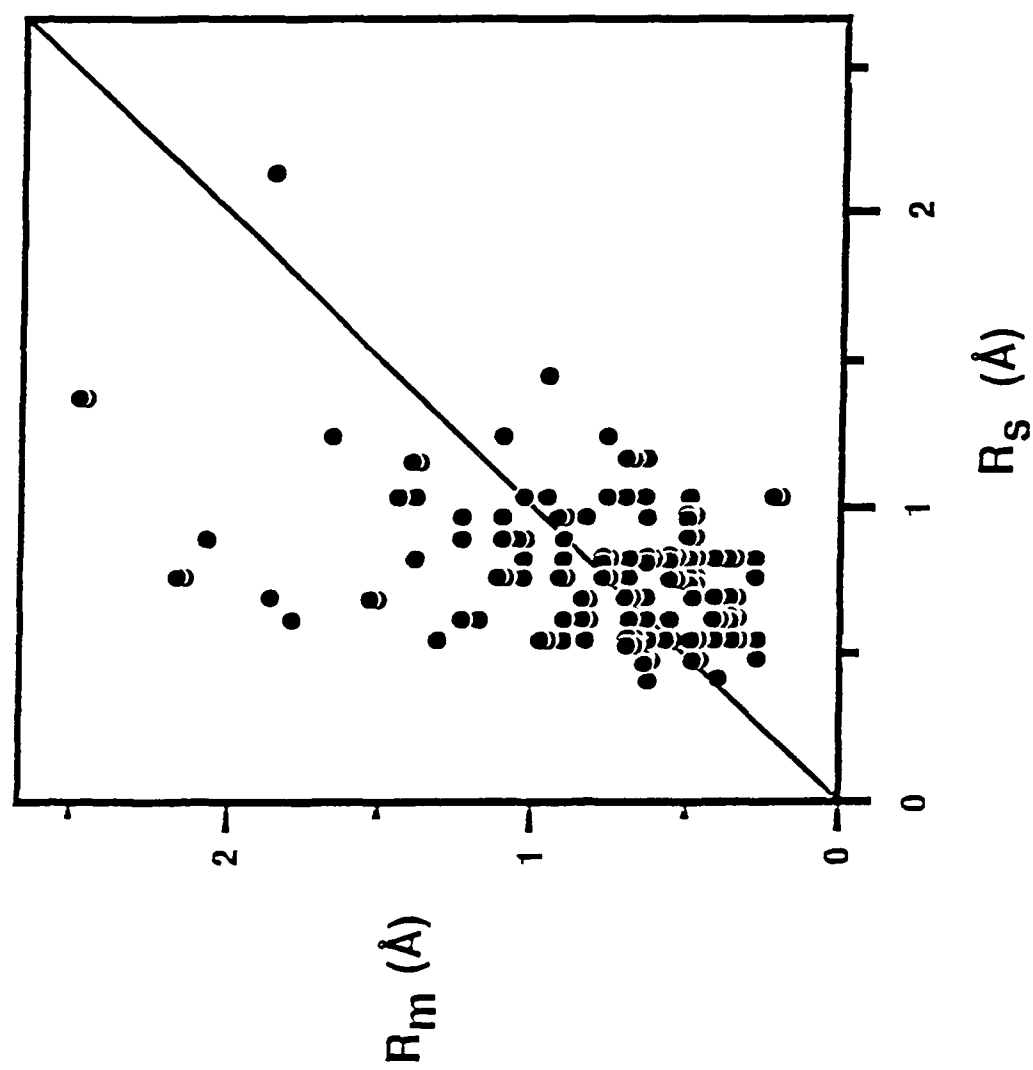
Figure 1. Schematic representation of the formation of
alkylsiloxane monolayers by adsorption of
alkyltrichlorosilanes ($R(CH_2)_nSiCl_3$, $n = 0 - 17$)
from solution onto silicon-silicon dioxide
(Si/SiO_2) substrates. The SiO_2 layer was
10 - 20 Å in thickness. The monolayers were
6 - 27 Å in thickness.

Scheme I. Methods for the syntheses of
alkyltrichlorosilanes.

Method A

$$RBr \xrightarrow[\text{2) SiCl}_4]{\text{1) Mg}} RSiCl_3 \quad \sim 50\ \%$$

Method B

$$RCH=CH_2 \xrightarrow[\text{cat. H}_2\text{PtCl}_6]{\text{HSiCl}_3} RCH_2CH_2SiCl_3 \quad \sim 70\ \%$$

Figure 2. Methyl-terminated alkylsiloxane monolayers prepared by adsorption of n-alkyltrichlorosilanes, $CH_3(CH_2)_nSiCl_3$, onto Si/SiO_2 substrates. Each data point represents measurements on a different silicon substrate. Usually monolayers containing a given chain length w're prepared in at least two independently constituted solutions of the alkyltrichlorosilane in bicyclohexyl or hexadecane. (A) Advancing contact angles, θ_a. The contact angles of water are above the dashed line; those of hexadecane are below. (B) Ellipsometric thicknesses (Å). The solid line represents the best linear least-squares fit for $n = 1 - 17$.

Figure: Plots of $\cos\theta_a$ and θ_a (A) and Length (Å) (B) versus n for $Si/SiO_2/O_3Si(CH_2)_nCH_3$.

Figure 3. XPS spectra of alkyltrichlorosilane monolayers, $R(CH_2)_9SiCl_3$ ($R = CH_3CH_2-$, $CH_2=CH-$, CH_3OCOCH_2-), on Si/SiO_2 substrates: survey spectra (left) and high resolution spectra of the carbon 1s (center) and silicon 2p (right) regions. The C 1s and Si 2p spectra are each normalized to the same maximum peak height.

Si 2p

Si

SiO₂
Si

C 1s

-CH₂-

-CO₂CH₃
-CO₂-
-C-

O 2s
Si 2p
Si 2s

C 1s

O 1s

-CH₃
-CH=CH₂
-CO₂CH₃

O (Auger, KLL)

Binding Energy (eV)

98   102   106   282   286   290   0   500   1000

Figure 4. Angle-dependent XPS survey spectra of a monolayer prepared by adsorption of octadecyltrichlorosilane ($CH_3(CH_2)_{17}SiCl_3$, OTS) onto an Si/SiO_2 substrate. Spectra were obtained at take-off angles of 90°, 35°, and 15°.

O (Auger, KLL) —

O 2s —
Si 2s —
Si 2p —

C 1s —

O 1s —

90°

35°

15°

Binding Energy (eV)

0

500

1000

Figure 5. Models for the binding of alkylsiloxane monolayers to Si/SiO2 substrates. (A) The silicon atom in the alkyltrichlorosilane, RSiCl3, forms three bonds to hydroxyl groups at the surface of the substrate oxide layer. The formation of this structure does not require any adsorbed water. (B) The silicon atom in RSiCl3 forms one or two bonds to surface hydroxyl groups. The remainder of the the Si-Cl bonds are hydrolyzed, resulting in the formation of silanols (-SiOH) and Si-O-Si linkages between adjacent alkylsilanes. The Si-O-Si links can also bind within the monolayer alkylsilanes whose silicon atom has not formed any bonds to the surface.

Figure 6. Ratio of the atomic intensities of the carbon 1s
(C) and silicon substrate 2p (Sub) peaks in XPS
for alkylsiloxane monolayers prepared from
$CH_3(CH_2)_nSiCl_3$. The intensity of the substrate is
a mathematical construct from the intensities of
the Si 2p, SiO_2 2p, and O 1s signals (see
appendix). The parameter C_∞/Sub_∞ is the ratio of
the volume atomic densities of crystalline silicon
and of carbon within crystalline hydrocarbons.
This parameter, C_∞/Sub_∞, is theoretically 0.8.
The function $\ln(C/Sub - C_\infty/Sub_\infty)$ is approximately
linear for $C_\infty/Sub_\infty \div 0.6 - 1.5$.

$$\ln\left[\frac{C}{Sub} - \frac{C_\infty}{Sub_\infty}\right]$$

Si/SiO$_2$/O$_3$Si(CH$_2$)$_n$CH$_3$

n

1.5 1.0 0.5 0 -0.5

0   4   8   12   16
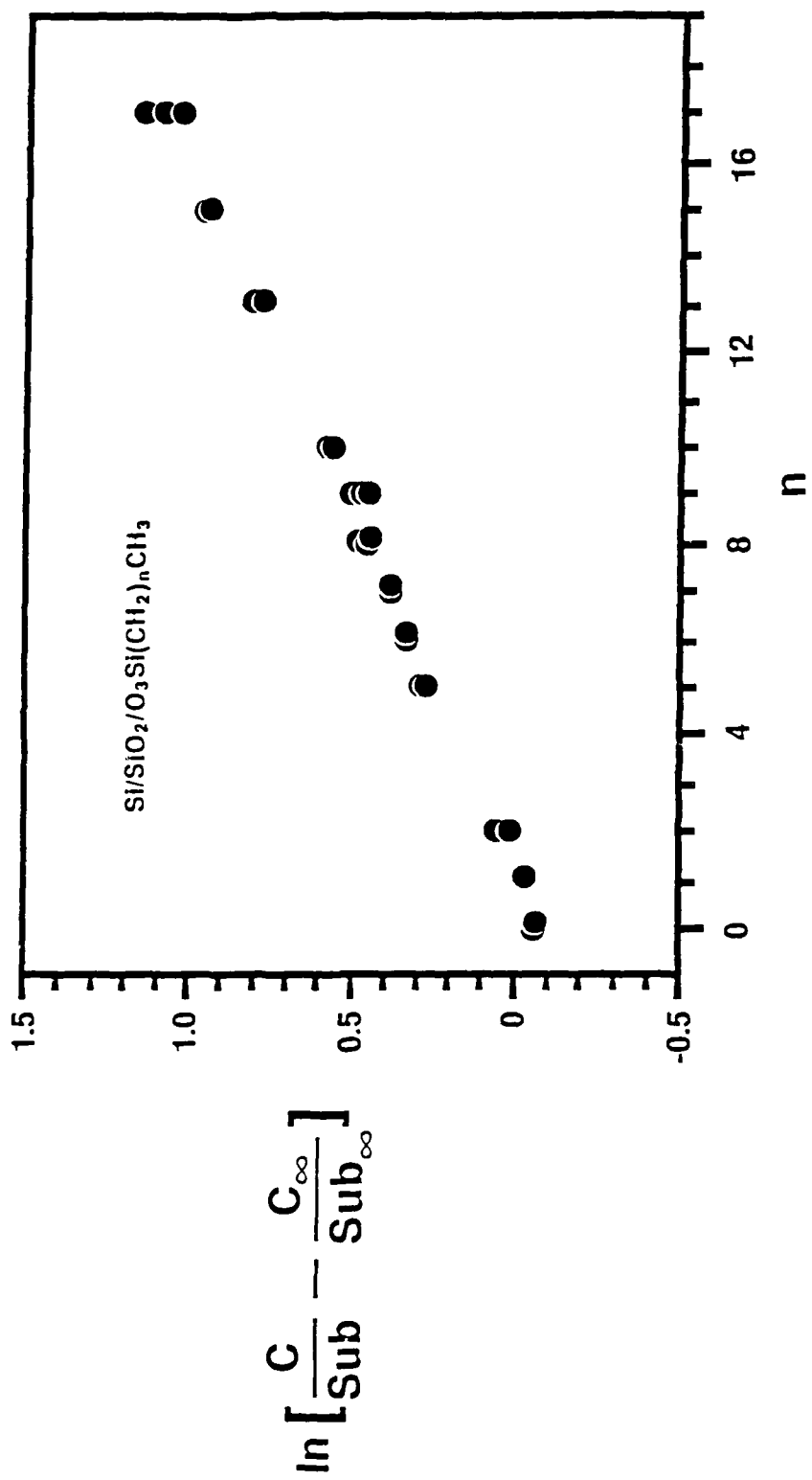
Figure 7. Kinetics of formation of an alkylsiloxane monolayer prepared from $CH_3(CH_2)_{13}SiCl_3$ (TTS) at 20 °C and 30% relative humidity. (A) Advancing contact angles of water and hexadecane. (B) Ellipsometric thicknesses. The calculated thickness for this monolayer, $L_{calculated}$ = 21.1 Å, is based on the assumption of a <u>trans</u>-extended conformation for the alkyl groups, with the chain axis perpendicular to the surface.

Figure 8. Stability of alkylsiloxane monolayers prepared from $CH_3(CH_2)_{13}SiCl_3$ (TTS) and exposed to 0.1 N HCl at 20 °C(○), 0.1 N NaOH at 20 °C (■), or hexadecane (●) at 75 °C. (A) Advancing contact angles. The contact angles of water are above the dashed line; those of hexadecane are below. (B) Ellipsometric thicknesses. The negative thickness after exposure to the 0.1 N NaOH probably indicates etching of the surface oxide after the monolayer had been removed.

Figure 9. Vinyl-terminated alkylsiloxane monolayers prepared by adsorption of $CH_2=CH(CH_2)_nSiCl_3$ (n = 4,9,15) onto Si/SiO_2 substrates. Each data point represents measurements on a different silicon substrate. (A) Advancing contact angles. The contact angles of water are above the dashed line; those of hexadecane are below. (B) Ellipsometric thicknesses (Å). The solid line represents the best linear least squares fit. The increment in thickness per methylene group is 1.44 Å.

Figure 10. Oxidation of methyl- and vinyl-terminated alkylsiloxane monolayers prepared from $CH_3(CH_2)_{13}SiCl_3$ ($\bigcirc$) and $CH_2=CH(CH_2)_{15}SiCl_3$ ($\bullet$) by $KMnO_4$ (0.5 mM) / $NaIO_4$ (19.5 mM) at 20 °C. The advancing contact angles of water (A) and ellipsometric thicknesses (B, in Å) were measured as a function of the time, T, of oxidation.
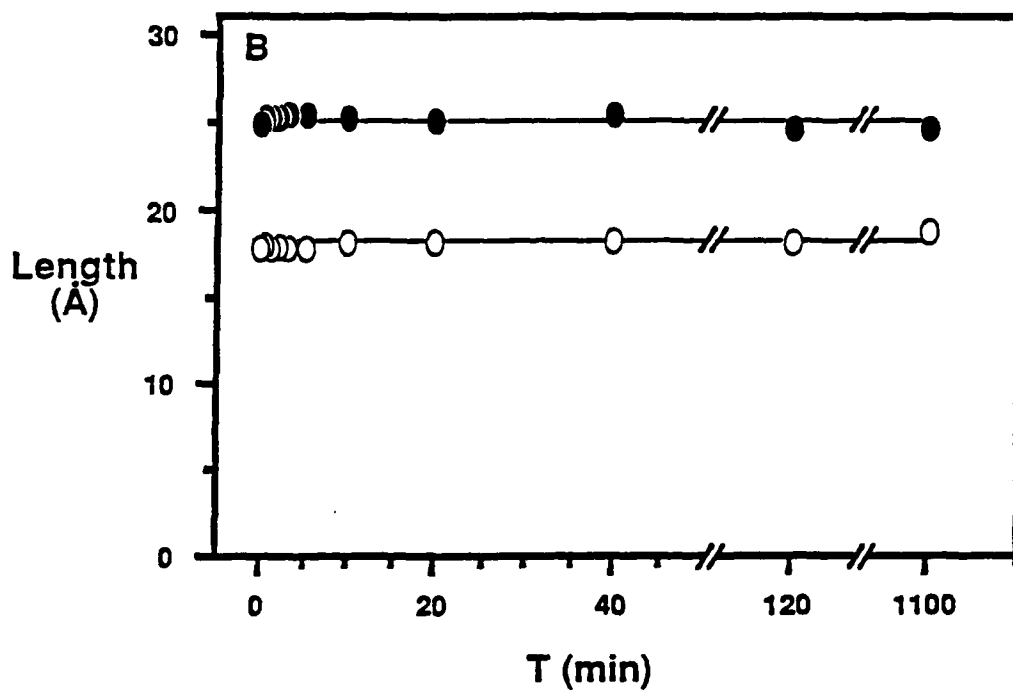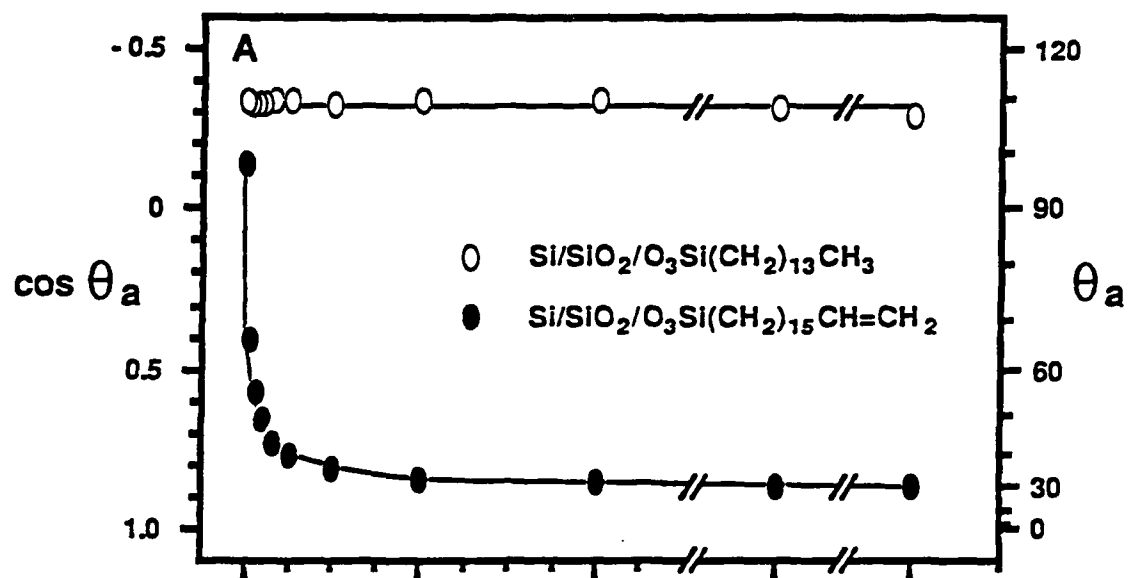
Figure 11. XPS spectra (survey and high resolution of the carbon 1s region) of reaction products from vinyl-terminated alkylsiloxane monolayers prepared from $CH_2=CH(CH_2)_nSiCl_3$ (n = 4, 9, 15): carboxylic acid from oxidation with $KMnO_4/NaIO_4$, alcohol from hydroboration (1. BH_3 2. $H_2O_2/NaOH$), and 1,2-dibromide (and related brominated species) from reaction with elemental bromine (Br_2). The C 1s spectra are normalized to the same maximum peak height. As n increases, the signal from the functionalized carbon atom(s) decreases relative to the signal from the methylene groups in the monolayer.
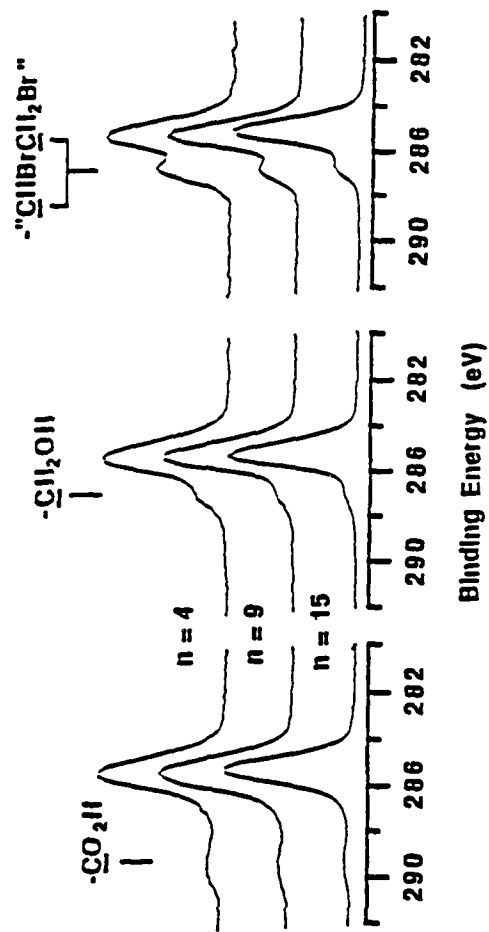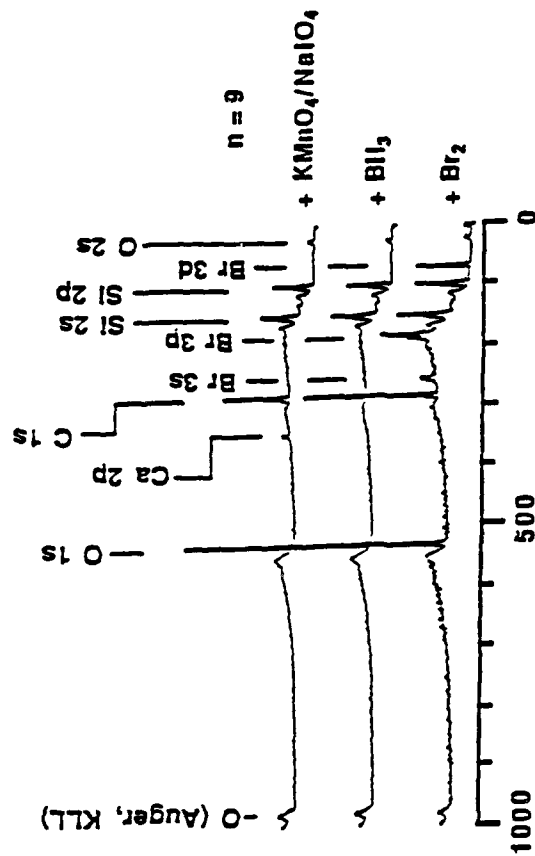
Si/SiO₂/O₃Si(CH₂)ₙCH=CH₂

n = 9

+ KMnO₄/NaIO₄

+ BH₃

+ Br₂

O 2s
Br 3d
Si 2p
Si 2s
Br 3p
Br 3s
C 1s
Ca 2p

O 1s

-O (Auger, KLL)

0   500   1000

-"CHBrCH₂Br"

-CH₂OH

-CO₂H

n = 4
n = 9
n = 15

Binding Energy (eV)

290 286 282
290 286 282
290 286 282

Figure 12. Reaction products from vinyl-terminated
alkylsiloxane monolayers prepared from
$CH_2=CH(CH_2)_nSiCl_3$ (n = 4, 9, 15): carboxylic
acid from oxidation with $KMnO_4/NaIO_4$ (O),
alcohol from hydroboration (1. BH_3 2. $H_2O_2/NaOH$)
(■), and 1,2-dibromide (and related brominated
species) from reaction with elemental bromine
(Br_2) (●). Each data point represents
measurements on a different substrate. The
markers represent typical errors in the
measurements of contact angles and ellipsometric
thicknesses. (A) Advancing contact angle of
water. (B) Change in ellipsometric thickness
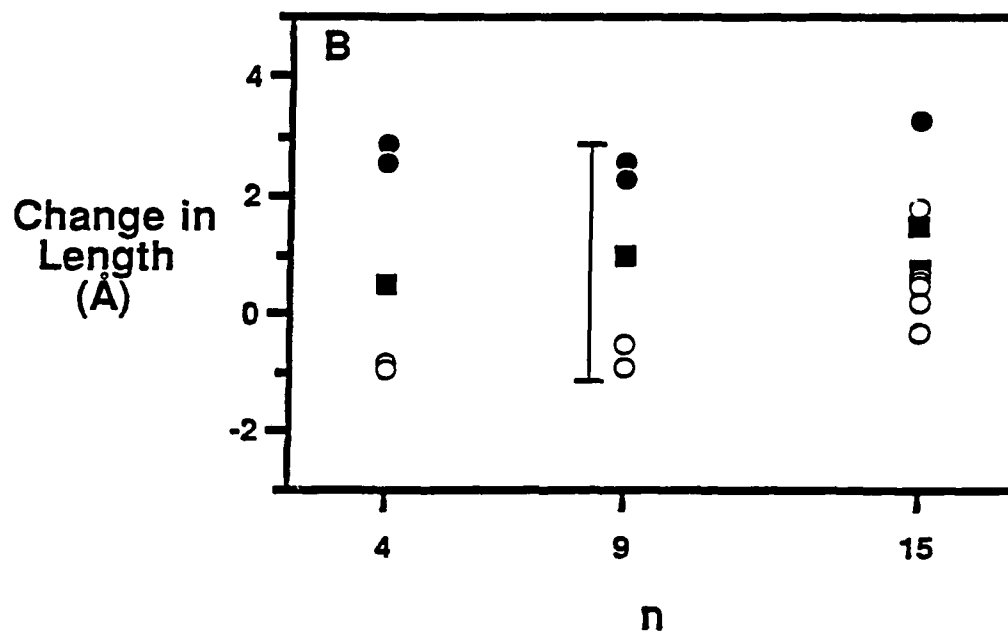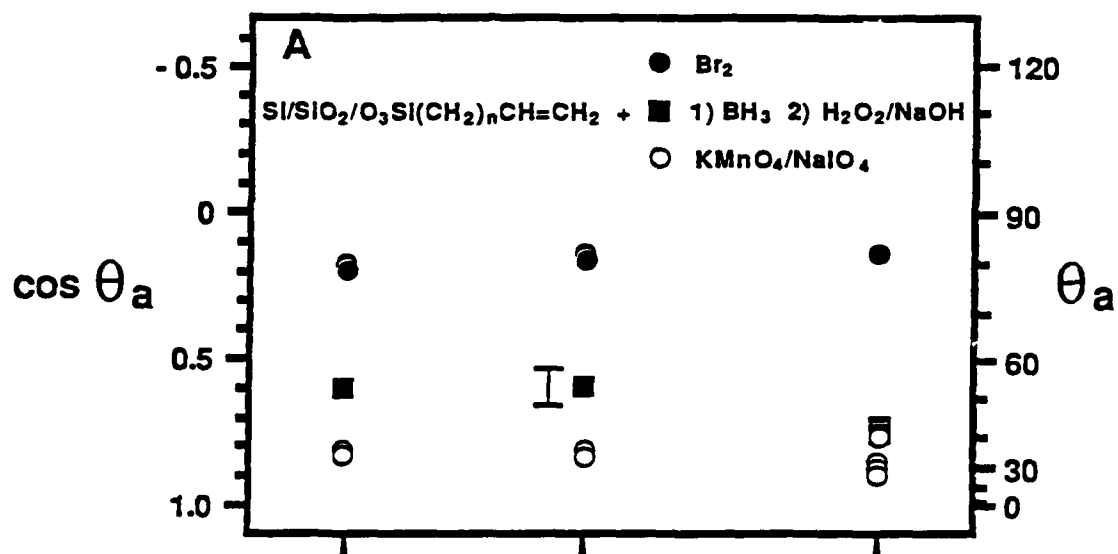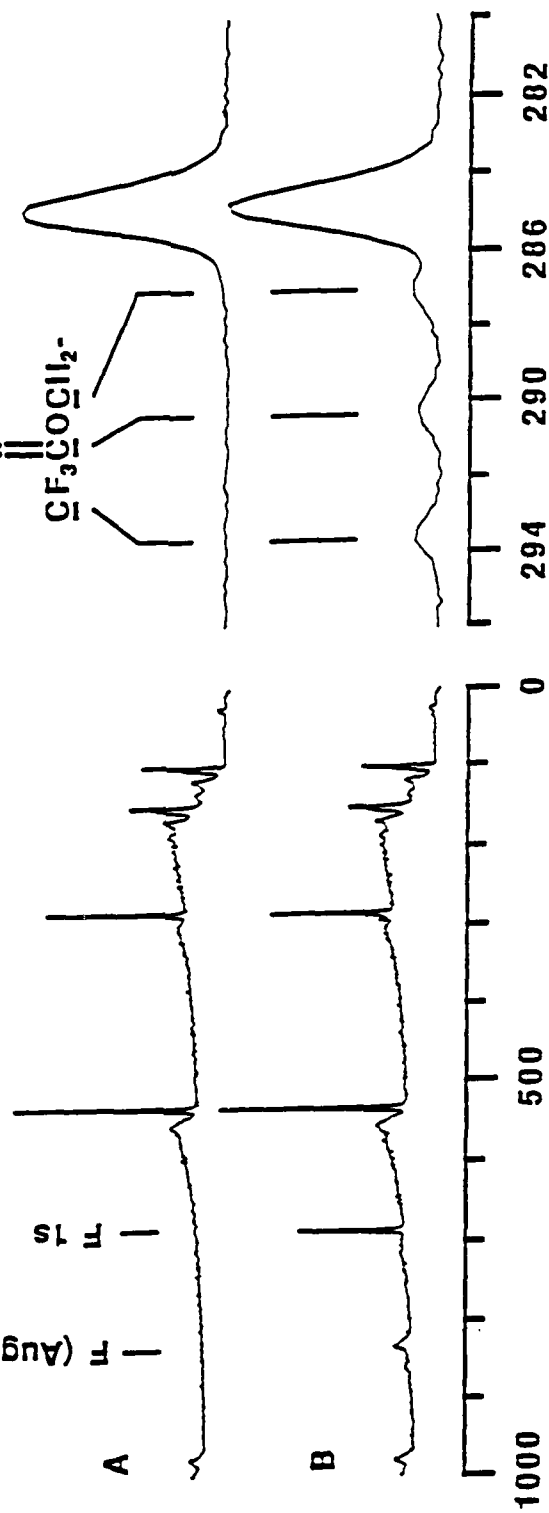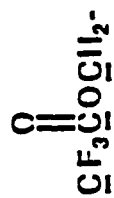(product minus reactant) of the monolayer as a
result of the surface reaction.

Figure 13. XPS spectra of alkylsiloxane monolayers prepared from $CH_2=CH(CH_2)_9SiCl_3$ and treated with trifluoroacetic anhydride (2% v:v in hexanes): survey (left) and high resolution of the carbon 1s region (right). The C 1s spectra are normalized to the same maximum peak height. (A) Vinyl-terminated monolayer. (B) Alcohol-terminated monolayer prepared from A by hydroboration (1. BH_3 2. H_2O_2/NaOH).

C 1s

$CF_3\underline{C}O\underline{C}H_2-$

$\overset{O}{\overset{||}{}}$

282 286 290 294

Binding Energy (eV)

Si/SiO$_2$/O$_3$Si(CH$_2$)$_9$CH=CH$_2$

0 500 1000

F 1s

F (Auger, KLL)

A

B

Figure 14. Extent of reaction within alkylsiloxane

monolayers: XPS spectra [survey (left), high

resolution of the carbon 1s (center) and bromine

3d regions (right)] of vinyl-, hydroxyl-, and

carboxylic acid-terminated monolayers prepared

from $CH_2=CH(CH_2)_{15}SiCl_3$ (HTS) and then

functionalized with elemental bromine (Br_2, 1%

in CH_2Cl_2). The C 1s and Br 3d spectra are each

normalized to the same maximum peak height. The

Br 3d spectra for B and C have been smoothed

using a nine-point algorithm with a symmetrical

triangle convolution function (Savitsky, A.;

Golay, M. J. E. Anal. Chem. **1964**, <u>36</u>, 1627-

1639). The dashed lines in the Br 3d spectra

for B and C represent the amount of bromine

remaining on these surfaces relative to A.

(A) "-CHBrCH₂Br"-terminated monolayer prepared

by bromination of the vinyl-terminated monolayer

prepared from HTS. (B) Bromination product of

the acid-terminated monolayer prepared by

oxidation with $KMnO_4/NaIO_4$ of a monolayer

prepared from HTS. This monolayer contained

both $-CO_2H$ and and "-CHBrCH₂Br" groups.

(C) Bromination product of the alcohol-

terminated monolayer prepared by hydroboration

(1. BH_3 2. H_2O_2/NaOH) of a monolayer prepared from HTS.   This monolayer contained both $-CH_2OH$ and "$-CHBrCH_2Br$" groups.   For A, B, and C "$-CHBrCH_2Br$" represents the 1,2-dibromide and related brominated species.

Br 3d

C 1s

Br 3d
Br 3p
Br 3s

A
B
C

1000   500   0   290   286   282   75   71   67
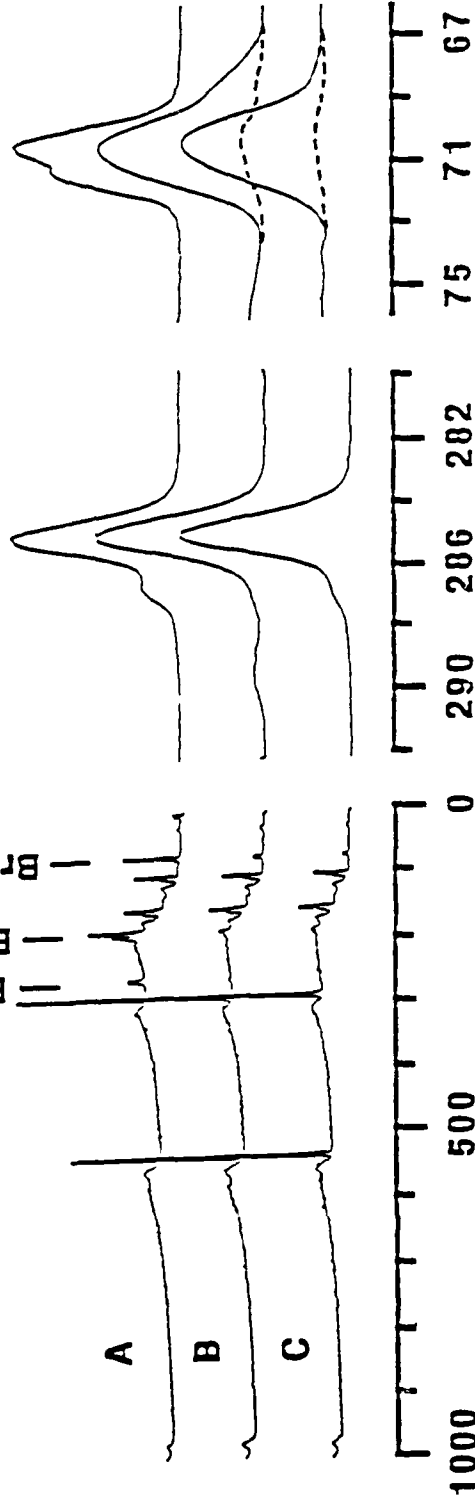
Binding Energy (eV)

Figure 15. Dependence of the advancing contact angle of

water, θ_a, on pH for alkylsiloxane monolayers:

methyl-terminated monolayer prepared from

$CH_3(CH_2)_{13}SiCl_3$ (■), vinyl-terminated monolayer

prepared from $CH_2=CH(CH_2)_{15}SiCl_3$ (HTS) (□),

methyl ester-terminated monolayer prepared from

$CH_3OCO(CH_2)_{10}SiCl_3$ (▲), alcohol-terminated

monolayer prepared by hydroboration of a

monolayer prepared from HTS (O), and acid-

terminated monolayer prepared by oxidation
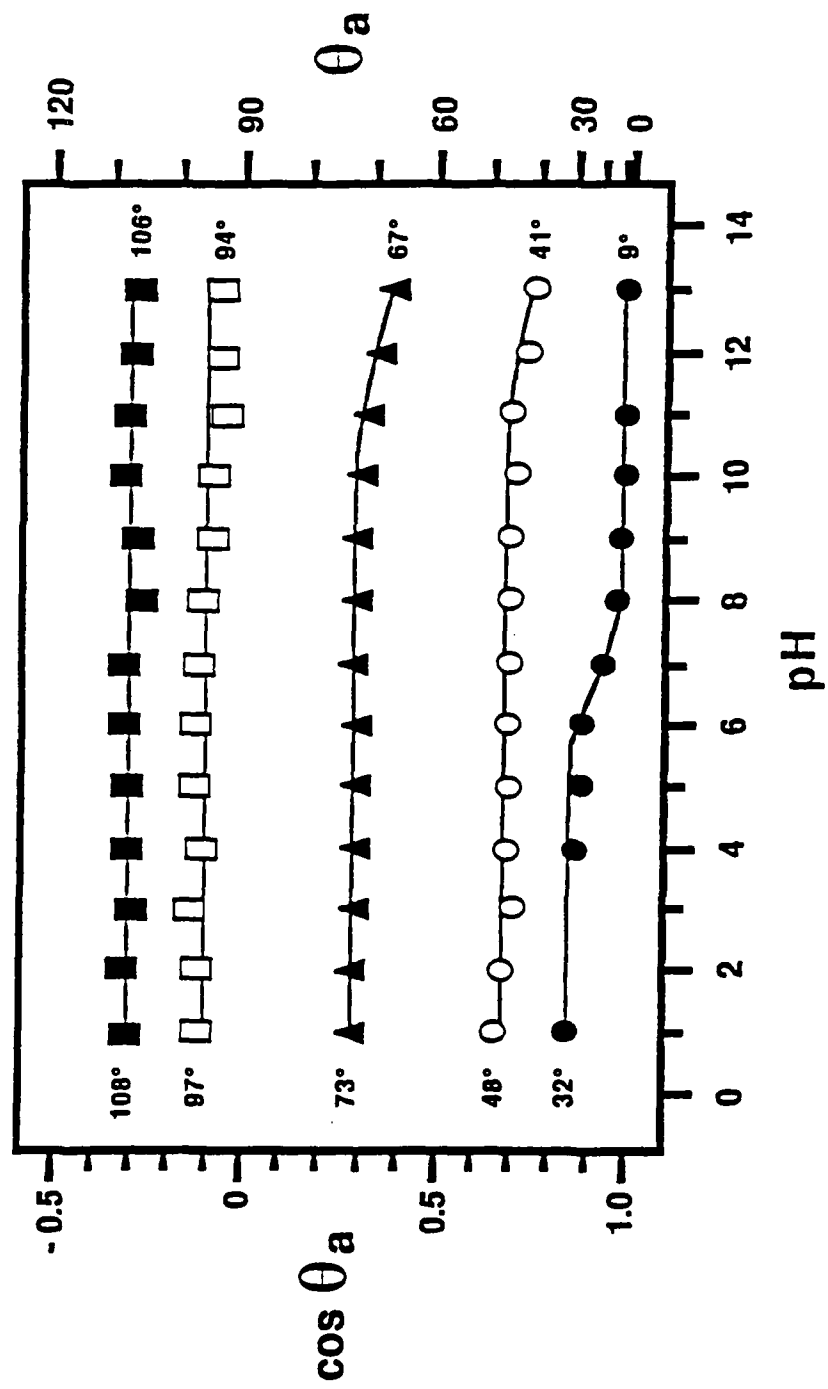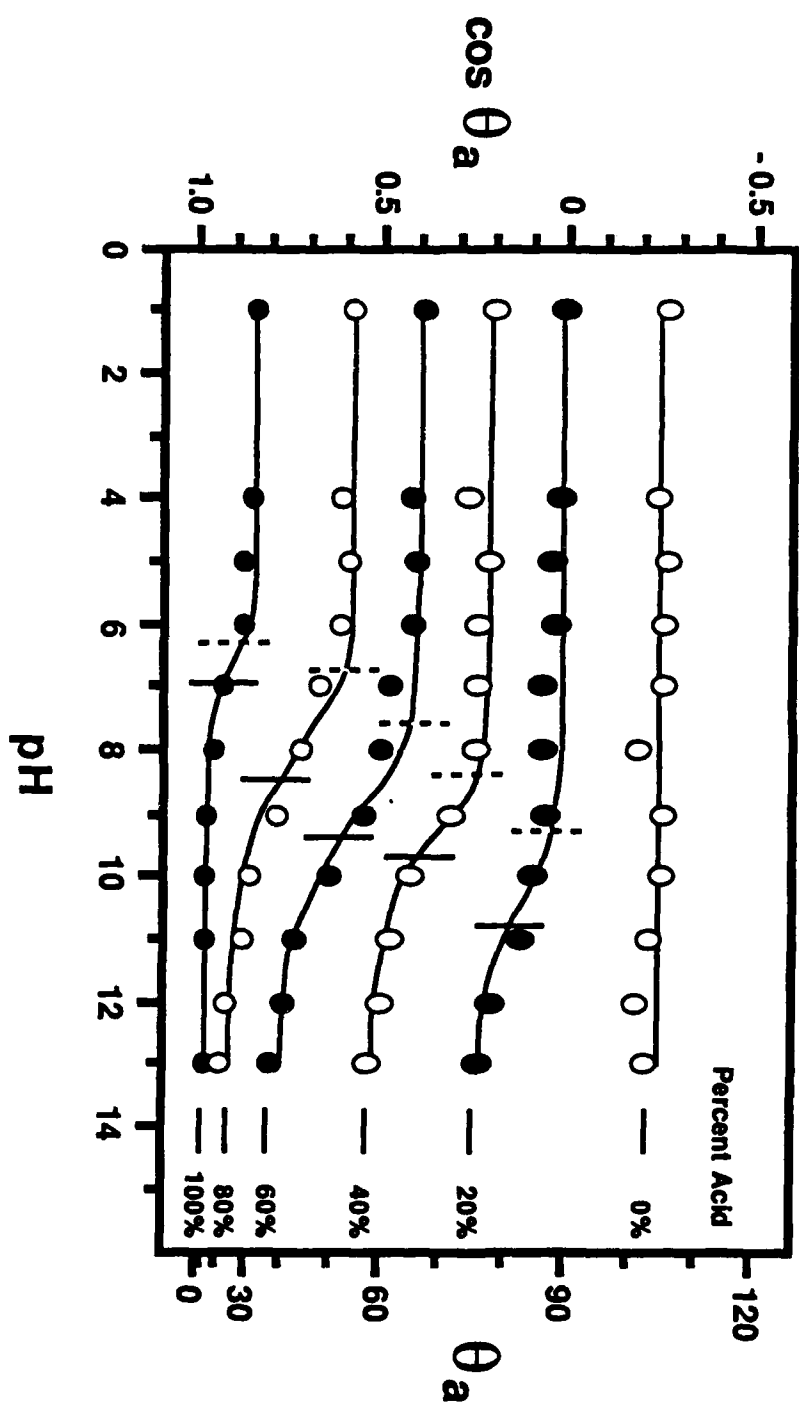
($KMnO_4/NaIO_4$) of a monolayer prepared from

HTS (●).

Figure 16. Dependence of the advancing contact angle of
water, θ_a, on pH for alkylsiloxane monolayers
that contained mixtures of terminal $-CH_3$ and
$-CO_2H$ groups. Monolayers were prepared by
adsorption from solutions that contained
$CH_2=CH(CH_2)_{15}SiCl_3$ and $CH_3(CH_2)_{15}SiCl_3$. The
percentages of the vinyl-terminated alkylsilane
in these solutions were 0, 20, 40, 60, 80, and
100%. The vinyl groups in these monolayers were
then oxidized to carboxylic acid moieties using
$KMnO_4/NaIO_4$. Based on the studies summarized in
Figure 14, the yield of these oxidations was
probably ~ 80%. The vertical lines represent
values of $pH_{1/2}$: the value of pH at which $\cos\theta_a$
is half-way between its high and low pH
extremes.

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