Alkyl Monolayers on Silicon Prepared from 1-Alkenes and Hydrogen-Terminated Silicon

Matthew R. Linford,[†] Paul Fenter,[‡] Peter M. Eisenberger,[‡] and Christopher E. D. Chidsey*,[†]

Contribution from the Department of Chemistry, Stanford University, Stanford, California 94305-5080, and Physics Department and Princeton Materials Institute, Princeton University, Princeton, New Jersey 08542

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Abstract: High-quality alkyl monolayers on silicon have been prepared from 1-alkenes and hydrogen-terminated Si(111). The 1-alkenes form monolayers upon free-radical initiation with diacyl peroxides. Heat also initiates monolayer formation, although monolayers prepared from heated long-chain 1-alkenes are of lower quality than those prepared with free-radical initiation. Even when a high concentration of diacyl peroxide is used to initiate monolayer formation, the 1-alkene is the primary constituent of the monolayer. Alkynes also form monolayers on silicon when initiated by diacyl-peroxides. X-ray reflectivity shows that the monolayer thickness is of molecular dimensions and that the density is close to that of crystalline hydrocarbons (~90%). Infrared spectroscopy shows that the alkyl chains in the monolayers are densely packed. Infrared dichroism shows that the chains are tilted from the surface normal and twisted about their axes. The wetting properties of the monolayers show that they are methyl terminated. After many weeks of air exposure, the silicon substrate under the monolayers is not significantly oxidized. The monolayers are very stable to boiling chloroform, boiling water, boiling acidic and basic solutions, and fluoride and are at least as stable as similar chain-length monolayers prepared from trichlorosilanes on oxidized silicon. We propose that alkyl chains in the monolayers are bound to the silicon substrate through silicon–carbon bonds and compare a proposed mechanism of bond formation to analogous homogeneous reactions.

Introduction

The surface of silicon has been studied intensively for many years because of its crucial importance in modern technology. Although thermal oxidation provides an effective passivation layer in most cases, applications may exist where this layer is inappropriate and different classes of thin films would be valuable for the chemical or electronic protection or modification of the interfacial properties of the material. A stable, densely-packed organic monolayer covalently bonded directly to the silicon surface would provide a technologically useful and controllable thin film.

Linford and Chidsey recently demonstrated that pyrolysis of neat diacyl peroxides in the presence of hydrogen-terminated silicon leads to the formation of monolayers, which they argued are covalently bonded directly to the silicon surface.[1] This was the first report of a densely-packed, organic monolayer on the silicon surface.[2,3] The monolayer thickness, chain packing, and wetting properties were like those of similar monolayers made from long-chain alkyl thiols on gold or from trichloro- or trialkoxy-alkylsilanes on oxidized silicon. However, infrared (IR) absorption spectra suggested the presence of some carbonyl groups which indicated that these monolayers were not comprised solely of alkyl chains. When exposed to boiling water, approximately 30% of the monolayer was removed. The carbonyl groups and this loss of material were attributed to the presence of hydrolyzable acyloxy bonds to the silicon surface ($Si-O-C(O)-CH_2-$) for ~30% of the chains, as well as more robust alkyl bonds to the silicon surface ($Si-CH_2-$) for the remaining ~70% of the chains.

This paper is a continuation of our on-going exploration of effective methods to prepare densely-packed monolayers directly on the silicon surface. Here we show that 1-alkenes can be employed to prepare monolayers on silicon. Both heat and free-radical initiators are used to initiate adsorption reactions. Neat olefins may have limited utility as they do not yield dense monolayers in all cases. However, the use of a mixture of an olefin and a diacyl peroxide readily yields monolayers that have IR spectra indicating solid-like packing of the alkyl chains and that are at least as stable as similar monolayers made from trichlorosilanes on oxidized silicon. X-ray reflectivity studies show that the chains are packed at approximately 90% the density of crystalline *n*-alkanes. X-ray reflectivity and IR dichroism indicate that the chains are tilted 35–45° from the surface normal. We propose a mechanism for monolayer formation from a mixture of an olefin and a diacyl peroxide on a silicon hydride surface by analogy with the known mechanism[4,5] of radical-mediated hydrosilylation of olefins with molecular silanes.

[†] Stanford University.

[‡] Princeton University.

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(2) Other workers have looked at the gas-phase reactivity of silicon with small carbon-containing molecules[3a] and also at the surface stabilization of the related semiconductors, Ge, InP, and GaAs by short-chain carbon species, surface alkylation by benzyl bromides, and long-chain alkyl thiols.[3b]

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Experimental Section

Materials. All chemicals were reagent grade or the highest available commercial grade and used as received unless otherwise specified. Ultrapure (18 MΩ·cm) water was obtained from a Millipore 4-bowl purification train and was used unless otherwise specified. Percentage compositions are by mass unless otherwise stated.

Other compounds were obtained as follows: 1-undecene (Aldrich, 99%), 1-dodecene (Aldrich, 95%), 1-hexadecene (Aldrich, 92%), 1-heptadecene (Aldrich, 99%), 1-dodecyne (Aldrich, 98%), 1-octadecene (Wiley, 95%), 1-undecyne (Wiley, 98%), 1-hexadecyne (Wiley, 97%), 1-dodecanonitrile (Lancaster, 98%), 1-chlorodecane (Aldrich, 98%), 11-bromo-1-undecene (Pfaltz and Bauer), octadecyltrichlorosilane (Aldrich, 95%), and $CD_3(CD_2)_{16}COOH$ (Cambridge Isotope Laboratories, 98% D).

All alkenes, all alkynes, dodecanonitrile, and 1-chlorodecane were distilled under reduced pressure (generally between 20 and 40 Torr) through a short path distillation apparatus prior to use, with the exception of 1-dodecene and 1-hexadecene which were distilled through a 6 in. Vigreaux column. Typically, the middle third of the fractional distillation was used.

Synthesis of Compounds. (a) Synthesis of 11-(chloro-1-undecene (CH_2=$CH(CH_2)_9Cl$). 11-Chloro-1-undecene was synthesized under phase-transfer conditions from 11-bromo-1-undecene following the synthesis of Sasson et al.[6] and distilled through a 6 in. Vigreaux column. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.78 (m, 1H), 4.94 (m, 2H), 3.53 (t, J = 6.8 Hz, 2H), 2.03 (m, 2H), 1.76 (m, 2H), 1.28 (m, 12H). Anal. Calcd for $C_{11}H_{21}Cl$: C, 70.00; H, 11.21; Cl, 18.78. Found: C, 70.33; H, 11.30; Cl, 18.42.

(b) Synthesis of Didodecanoyl Peroxide $[CH_3(CH_2)_{10}C(O)O]_2$. (All diacyl peroxide syntheses were based on a modified procedure of Fieser and Oxford.[7]) Dodecanoic acid (25 g) (Aldrich, 99.5+%) and thionyl chloride (32 mL) (Aldrich, 99+%) were held at reflux for 2 h. Unreacted $SOCl_2$ was then removed by evaporation at reduced pressure and the resultant acid chloride was dissolved in 360 mL of diethyl ether and added to an ice-cooled solution of 420 mL of water, 116 g of 30% aqueous H_2O_2, and 82 g of NaOH in a 2 L separation funnel. Small amounts of ice were added followed by vigorous shaking every minute for the first 3 min of the procedure and every 2−3 min thereafter, to make a total of 12 min of vigorous shaking. The reaction mixture was extracted with 250 mL of hexane and the organic phase was extracted 3 times with 100 mL of 1 M NaOH and finally washed with water until the water was neutral. The hexane was removed by rotary evaporation. The solid, white product was dissolved in ~2 L of absolute ethanol at 60 °C and cooled to room temperature. The crystalline precipitate that formed was collected by filtration and dried. Yield: 55−65%.

Longer diacyl peroxides were similarly prepared with similar yields from hexadecanoic and octadecanoic acid (Aldrich) with the exception that the desired diacyl peroxides precipitated upon formation and were collected by filtration, washed, and recrystallized from ~2 L of absolute ethanol at 65 °C.

$[CD_3(CD_2)_{16}C(O)O]_2$ was prepared from perdeuterated octadecanoic acid.

(c) $[CH_3(CH_2)_{16}C(O)O]_2$: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.42 (t, J = 7.6 Hz, 4H), 1.71 (m, 4H), 1.25 (m, 56H), 0.88 (t, J = 6.8 Hz, 6H); IR (melt, cm^{-1}) 2914.9 (s) ($\nu_a(CH_2)$), 2850.3 (s) ($\nu_s(CH_2)$), 1806.1 (m)/1776.2 (s) (coupled C=O groups). Anal. Calcd for $C_{36}H_{70}O_4$: C, 76.27; H, 12.44. Found: C, 76.17; H, 12.55. Large quantities of gas were evolved with heating to ~100 °C.

(d) $[CH_3(CH_2)_{14}C(O)O]_2$: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.42 (t, J = 7.5 Hz, 4H), 1.71 (m, 4H), 1.25 (m, 48H), 0.88 (t, J = 6.7 Hz, 6H). Anal. Calcd for $C_{32}H_{62}O_4$: C, 75.24; H, 12.23. Found: C, 75.51; H, 12.44. Large quantities of gas when heated to ~100 °C.

(e) $[CH_3(CH_2)_{10}C(O)O]_2$: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.42 (t, J = 7.5 Hz, 4H), 1.71 (m, 4H), 1.25 (m, 32H), 0.88 (t, J = 6.8 Hz, 6H) Anal. Calcd for $C_{24}H_{46}O_4$: C, 72.31; H, 11.63. Found: C, 72.38; H, 11.81. Large quantities of gas were evolved with heating to ~100 °C.

Preparation of Oxidized Silicon and Silicon−Hydride Surfaces. The silicon substrates were either shards of silicon wafers (Si(111), Monsanto, n-type) or Si(111) trapezoidal plates designed for attenuated total internal reflection spectroscopy (ATR plates) (Harrick Scientific, 45°, 50 × 20 × 1 mm). All cleaning and etching of the silicon surfaces was performed in 30 mL capped fluorocarbon vials.

(a) Oxidized Silicon. ***Caution:*** *The basic and acidic solutions of hydrogen peroxide described in this procedure are exceedingly dangerous, particularly around organic materials, and should be handled with great care.* Silicon surfaces were cleaned for 2 h in ~100 °C 3:1 H_2SO_4(conc):30% H_2O_2, by volume, for 15 min in 1:1 30% NH_4OH:30% H_2O_2,[8] by volume, and finally for ~30 min in 3:1 H_2SO_4(conc):30% H_2O_2, by volume. The silicon was rinsed thoroughly with water between and after each cleaning.

(b) Silicon Hydride. To generate the H−Si(111) surface, the oxidized silicon was dried with an inert gas and immersed in an aqueous solution of 40% NH_4F for 4 min.[1,9,10] These etching conditions have been shown to create a hydrogen-terminated silicon surface with hydrogens bonded perpendicular to the surface and with a defect density of ~0.5%.[10] The resulting hydrophobic surface was rinsed with flowing water for 30 s on each side.

Preparation of Monolayers. (a) Monolayer Synthesized from $CH_3(CH_2)_{17}SiCl_3$ on Oxidized Silicon. A clean, oxidized silicon shard was dried in flowing N_2 or Ar and put in a solution made from 20 mL dry isooctane, 5 mL of dry CCl_4, and 20 μL of distilled octadecyltrichlorosilane.[11] The surface was removed after ~48 h and rinsed with hexane, 2-propanol, and water. It was then cleaned with an aqueous sodium dodecyl sulfate solution using a camel hair brush and finally rinsed with water and dried.

(b) Monolayer Made from Neat $[CH_3(CH_2)_{16}C(O)O]_2$ on Si(111). ***Caution:*** *To reduce the risk of explosion, it is imperative that all reactions which employ the pyrolysis of diacyl peroxides be performed in vented reaction vessels, e.g., a vessel connected to a mineral oil bubbler.* $[CH_3(CH_2)_{16}C(O)O]_2$ (2−3 g) was melted at ~75 °C under vacuum (P < 20 mTorr) in a narrow quartz cuvette (inner dimensions: ~22 × 55 × 3 mm), and then the cuvette was backfilled with argon. A freshly prepared, dry, fluoride ion-etched silicon hydride surface was placed in the still molten material. The cuvette was reevacuated, flooded with argon, vented to a bubbler, and heated to 100 °C. Vigorous gas evolution occurred for the first ~10 min. After 1 h, the resulting hydrophobic surface was removed and rinsed repeatedly with ethanol and hexane to remove physisorbed material, sonicated twice for 5 min each in fresh portions of CH_2Cl_2, and finally rinsed briefly with ethanol and dried in a stream of inert gas.

(c) Monolayer Made from 10% $[CH_3(CH_2)_{16}C(O)O]_2$ and 90% $CH_3(CH_2)_{15}CH$=CH_2 on Si(111). 1-octadecene (1.8 g) and $[CH_3(CH_2)_{16}C(O)O]_2$ (0.2 g) were heated to 70 °C under vacuum (P < 20 mTorr) in a quartz cuvette until all the diacyl peroxide dissolved and then the cuvette was backfilled with argon. A freshly prepared, dry, fluoride ion-etched silicon hydride surface was then placed in the liquid. The cuvette was reevacuated, flooded with argon, vented to a bubbler, and heated to 100 °C for 1 h during which time gas evolution was observed. The sample was then removed and rinsed repeatedly with ethanol and hexane to remove physisorbed material, sonicated twice for 5 min in CH_2Cl_2, and finally rinsed briefly with ethanol and dried in a stream of inert gas.

(d) Monolayer Made From $CH_3(CH_2)_{15}CH$=CH_2 on Si(111). 1-Octadecene (2 g) was placed in a quartz cuvette and degassed by bubbling Ar through it for at least 1 h. A freshly prepared, dry, fluoride ion-etched silicon hydride surface was then placed in the liquid. The cuvette was evacuated, flooded with argon, vented to a bubbler, and heated to 100 150, or 200 °C for 1 h. The sample was then removed and rinsed repeatedly with ethanol and hexane to remove physisorbed

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(9) Higashi and Chabal recommend that Si(111) be etched for 6.5 min with 40% aqueous NH_4F to make the "ideally hydrogen-terminated surface.[10]" We find that 6.5-min etches progressively damage the bevels of the ATR plates and attenuate light passage through them. We cannot distinguish the FTIR spectra of hydrogen-terminated silicon made with 4- and 6.5-min etches and find that 4-min etches cause much less damage to the ATR plates.

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material, sonicated twice for 5 min in CH_2Cl_2, and finally rinsed briefly with ethanol and dried in a stream of inert gas.

Monolayer Stability Tests. Stability tests were performed using water, chloroform, 10% 1 M aqueous NH_4OH in 90% dioxane (by volume), 10% 2.5 M aqueous H_2SO_4 in 90% dioxane (by volume), and 48% aqueous HF. With the exception of the HF solution, which was used at room temperature, the other solvents or solutions were brought to reflux with a reflux condenser after which the monolayers were immersed for the time indicated in the text, rinsed with ethanol, dried, and characterized as described.

Contact Angle Goniometry. Contact angles of both water and hexadecane were measured with a Rame-Hart Model 100 goniometer at the ambient temperature and humidity. A drop of liquid ($\sim 1\ \mu L$) on the surface was expanded by addition of liquid through an immersed 22-gauge flat-end stainless steel needle. The advancing contact angle was measured immediately. The receding contact angle was measured immediately after removing liquid from the drop and observing the drop's area of contact with the surface to decrease. At least four measurements of the advancing and receding contact angles of water and hexadecane were made for each surface. The advancing contact angles were generally within ±1° of the reported average although some ranged as high as ±2°. The receding contact angles were generally within ±2° of the reported average although a few were as high as ±4°. The accuracy of the method tends to decrease as the contact angle becomes smaller. These errors in the advancing water and hexadecane contact angles are small enough to easily distinguish between methyl-terminated surfaces and polymethylene surfaces, which are reported to have advancing water contact angles of 111−115° and 102−103°, respectively, and advancing hexadecane contact angles of 45−46° and <10°, respectively.[12]

Ellipsometry. Ellipsometric measurements were made with a Gaertner Variable Angle Ellipsometer L116B using a helium−neon laser and an incident angle of 70°. Automatic ellipsometry programs from Gaertner were used to calculate film thicknesses. An index of refraction of 1.46 was used for the films. This value is convenient as it is the refractive index of silicon dioxide, with which the accuracy of the instrument is verified, and is in the range of values appropriate to saturated hydrocarbon phases.[13,14] Effective substrate optical constants were measured for freshly prepared hydrogen-terminated silicon and oxidized silicon. In general, the thicknesses of at least 3 different points on each surface were measured and found to be within ±1 Å of the reported average. Sample to sample reproducibility is ±2 Å.

Although the absolute accuracy of ellipsometry can be questioned, we have found it to be a quick, useful, and reproducible assay of relative surface coverage. For example, the monolayer formed from 10% $[CH_3(CH_2)_{16}C(O)O]_2$ and 90% $CH_3(CH_2)_{15}CH{=}CH_2$ has been prepared many times on different H−Si(111) surfaces. Its thickness by ellipsometry has always been found to be 21 ± 2Å.

Infrared Spectroscopy. Infrared spectra were obtained with the aforementioned silicon ATR plates using a Mattson model RS-10000 research grade spectrometer and additional external optics. Individual, s- and p-polarized attenuated total internal reflection spectra were collected for the oxidized silicon, silicon hydride, and monolayer surfaces at 2 cm^{-1} resolution. Light was focused onto one of the 45° bevels of the ATR plate. The plate rested on three steel balls and against three cylindrical posts to allow reproducible positioning. After exiting the crystal, the IR light was directed into a mercury cadmium telluride (MCT) detector (Graseby Infrared) with an associated preamp. The resultant signal was returned to the spectrometer. The external optics were surrounded by a Plexiglas box which was purged with filtered, water- and carbon dioxide-depleted air (Balston 74-5041 Pure Air Generator). Monolayer intensity spectra were ratioed with that of the freshly oxidized silicon ATR plate to get transmission spectra from which absorption spectra were obtained. In some cases, a linear background was subtracted from the absorption spectra. The reproducibility of peak positions and absorptions in nominally identical samples was found to be ±0.5 cm^{-1} and ±0.005, respectively.

The dichroic ratio, D, is defined as the ratio of the intensities of the s-polarized absorbance, $A^{\text{s-pol}}$, to p-polarized absorbance, $A^{\text{p-pol}}$, of a particular IR peak: $D = A^{\text{s-pol}}/A^{\text{p-pol}}$. From this ratio, one can obtain information about molecular orientation. The dichroic ratios of the symmetric and asymmetric methylene stretches were used to calculate the angles between these transition dipole moments and the surface normal (α_s and α_a, respectively) following the procedure developed by Harrick,[15a] Haller,[15b] and Ulman.[16] These angles allow us to find both the chain tilt angle, θ ($\cos^2\theta = 1 - \cos^2\alpha_s - \cos^2\alpha_a$), and the chain twist angle, γ ($\cos\gamma = \cos\alpha_s/\sin\theta$), assuming that the chain has an all-trans configuration.

We note that the dependence of the dichroic ratio on the angle between the transition dipole moment and the surface normal (α) is very steep in the regions around $D = 1$ and 0.[16] Therefore, a small change in D in these regions leads to a large apparent change in the calculated α, and care must be exercised in interpreting such data. For instance, for the dichroic ratio of the asymmetric methylene stretch ($\nu_a(CH_2)$) of nominally equivalent monolayers prepared from octadecyltrichlorosilane on oxidized silicon, Sagiv reports values of 1.03 and 1.09.[17] Ulman reports 1.04[16] and we find a value of 1.08. These small changes in D result in values of α_a from 70° to 83°. In this work, most values of D are close to 1 and so the resulting tilt and twist angles have relatively large errors associated with them, which may be as large as ±10°. Nevertheless, Table 2 shows a qualitative correlation between chain tilt and ellipsometric thickness.

X-ray Photoelectron Spectroscopy (XPS). X-ray photoelectron spectra were obtained on a Surface Science Model 150 XPS spectrometer equipped with an Al Kα source, quartz monochromator, concentric hemispherical analyzer, and a multichannel detector. No electron flood gun was employed. The pressure in the analytical chamber during analysis was approximately 5×10^{-8} Torr. A take-off angle of 35° from the surface was used. Spectra of C(1s) (275−295 eV binding energy), O(1s) (525−545 eV binding energy), F(1s) (675−695 eV binding energy), Si(2p) (90−110 eV binding energy), and Cl(2p) (190−210 eV binding energy) as well as survey scans (0−1100 eV binding energy) were recorded with a 250 × 1000 μm spot size. The areas under the unsmoothed peaks were measured after a Shirley background subtraction and corrected for the number of scans.

In the analysis of chlorine-terminated monolayers, C(1s) signals from the monolayer were corrected for photoelectron attenuation,[18] except in the control monolayer. Atomic sensitivity factors of 0.296 and 0.891 were used for carbon and chlorine, respectively.[19]

X-ray Reflectivity. X-ray specular reflectivity has been previously employed as a technique to study the structures of surfaces and thin films.[20,21] In brief, the x-ray specular reflectivity of a multilayer structure contains interference terms due to scattering at the interfaces between materials of differing electron density. Consequently, it is directly sensitive to the electron density profile, e.g., thickness, electron density, and roughness of each of the individual layers, and is not sensitive to the two-dimensional molecular order within the monolayer film. In the case of a monolayer at the surface of a semi-infinite substrate, the expression for the specular reflectivity acquires a particularly simple form, and can be written as:[20]

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$$R = R^*_{\mathrm{f}}\left|(1 - x)\exp\left(\frac{-Q_z^{\,2}\sigma_0^{\,2}}{2}\right) + x\exp\left(\frac{-Q_z^{\,2}\sigma_{\mathrm{ml}}^{\,2}}{2}\right)\exp(iQ_zL)\right|^2$$

R_{f} is the Fresnel reflectivity from an isolated interface ($R_{\mathrm{f}} \propto 1/Q_z^4$). $x = \varrho_{\mathrm{ml}}/\varrho_{\mathrm{o}}$, where ϱ_{ml} and ϱ_{o} are the electron densities of the monolayer and substrate, respectively, and we have fixed $\varrho_{\mathrm{o}} = 0.70$ e$^-$/Å^3.[20] σ_{ml} and σ_{o} are the monolayer and substrate roughnesses, respectively. L is the thickness of the monolayer, and Q_z is the momentum transfer ($Q_z = (4\pi/\lambda)\sin(2\theta/2)$), where 2θ is the X-ray scattering angle. Due to interference between the X-rays scattered from the monolayer−gas and monolayer−substrate interfaces, minima in the reflectivity can be observed to occur at $Q_z = (2n + 1)\pi/L$; the depth and position of these minima then provide a direct measure of the density and thickness of the monolayer film. The uncertainties given in the results section of these derived quantities are determined by either the sample to sample variation (in the case of the hydride surface) or the statistical uncertainty in the parameter through a least-squares fitting analysis.[22]

The X-ray specular reflectivity data were obtained using Cu Kα radiation ($\lambda = 1.54$ Å) from a rotating-anode source; a pyrolitic graphite crystal was used as a monochromator. We note that while it is always preferable to have a larger data set which could be obtained with a brighter light source, i.e. a synchrotron, the data obtained here with a rotating anode are sufficient to measure the thickness and density of the film.

For these measurements, the sample was held in a He-filled cell to avoid the possibility of beam damage or contamination through air exposure. The specular scattering intensity was determined by subtracting the non-specular intensity (measured by offsetting the sample by ±0.6°) from that measured in the specular condition. The size of the X-ray beam was adjusted to optimize the specular signal; in the small angle regime, the X-ray beam had a size of 0.2 mm × 2 mm, while for large angles (i.e., $2\theta > 5°$) the beam size was 1.3 mm × 2 mm.

Results

Figure 1 compares the C−H stretching regions of attenuated total reflection infrared (ATR-IR) absorption spectra of monolayers formed on H−Si(111) from 100% $[CH_3(CH_2)_{16}C(O)O]_2$, from 100% $CH_3(CH_2)_{15}CH{=}CH_2$, and from 90% $CH_3(CH_2)_{15}CH{=}CH_2$ and 10% $[CH_3(CH_2)_{16}C(O)O]_2$. The monolayer formed from 100% $[CH_3(CH_2)_{16}C(O)O]_2$ has been described previously.[1] This film was shown to compare very favorably by ellipsometry, IR, and wetting to monolayers formed from methyl-terminated thiols on gold and alkyltrichlorosilanes on oxidized silicon (see Table 1). The asymmetric methylene stretch of this monolayer indicates that the chains have a solid-like packing[23,24] as do monolayers formed from octadecyltrichlorosilane and octadecanethiol on oxidized silicon and gold, respectively (see Table 1). A small peak at about 1700 cm^{-1} in the IR spectra (see inset to Figure 1) was attributed to an acyloxy linkage to silicon (Si−O−C(O)−), which accounted for approximately 30% of the monolayer.[1,25,26]

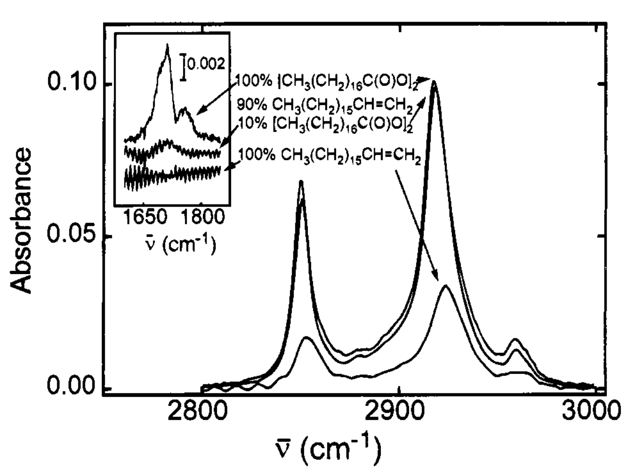

Figure 1. C−H and carbonyl stretching regions of infrared absorption spectra (p-polarized) of monolayers prepared at 100 °C from 100% $[CH_3(CH_2)_{16}C(O)O]_2$, 90% $CH_3(CH_2)_{15}CH{=}CH_2$ and 10% $[CH_3(CH_2)_{16}C(O)O]_2$, and 100% $CH_3(CH_2)_{15}CH{=}CH_2$.

Figure 1 also shows the monolayer formed by simply heating H−Si(111) in the presence of $CH_3(CH_2)_{15}CH{=}CH_2$ to 100 °C for 1 h. This film has high water and hexadecane contact angles, which suggests that it is a fairly uniform methyl-terminated surface (see Table 1).[12] However, the IR spectrum of this monolayer suggests its structure is closer to that of a liquid than a solid alkane ($\nu_a(CH_2) = 2923$ cm^{-1}).[23] Figure 2 and Table 1 show that heating H−Si(111) to progressively higher temperatures in the presence of the neat olefin leads to higher coverages and densities, as indicated by the shifts in IR peak intensities and positions. However, even at 200 °C, the coverage and density are lower than those obtained with the neat diacyl peroxide at 100 °C (see Table 1).

Returning to Figure 1, we now consider the film formed by heating H−Si(111) to 100 °C in a mixture of 90% $CH_3(CH_2)_{15}CH{=}CH_2$ and 10% $[CH_3(CH_2)_{16}C(O)O]_2$. The monolayer prepared from this combination of reagents has virtually the same asymmetric methylene stretching mode as the monolayer prepared from 100% $[CH_3(CH_2)_{16}C(O)O]_2$ (see Figure 1). Also, as was observed for monolayers prepared from 100% $[CH_3(CH_2)_{16}C(O)O]_2$, the Si−H stretch characteristic of H−Si(111) disappears and an increase in absorbance from 3000 to 3700 cm^{-1} suggests the formation of SiOH groups.[27,28] Table 1 shows that the wetting properties of the monolayer prepared from 90% $CH_3(CH_2)_{15}CH{=}CH_2$ and 10% $[CH_3(CH_2)_{16}C(O)O]_2$ and from 100% $[CH_3(CH_2)_{16}C(O)O]_2$ are virtually identical. These data might suggest that the olefin functions only as a solvent in this monolayer preparation. However, its role as a reactant is indicated by the substantial decrease in carbonyl absorption seen in the inset to Figure 1, suggesting that a significant fraction of the chains may be derived from the olefin.

Deuterium Labeling of Diacyl Peroxide. To establish that monolayers formed from mixtures of olefins and diacyl peroxides are composed largely of alkyl chains derived from the olefin, we performed a labeling study to unambiguously demonstrate the level of incorporation of each molecule into the monolayer. Figure 3 shows the CH_2 and CD_2 IR stretching regions of monolayers formed from 90% $CH_3(CH_2)_{15}CH{=}CH_2$

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[22] Bevington, P. R. *Data Reduction and Error Analysis for the Physical Sciences*; McGraw-Hill: New York, 1969.

[23] It has been observed in the IR spectroscopy of homologous series of alkanes and their derivatives that the asymmetric methylene stretch of a solid alkane occurs 6−8 cm^{-1} below that of the liquid alkane.[13,24] Because of the ease with which monolayer infrared spectra can be obtained, this correlation provides an important method of assessing the solid- or liquid-like packing of alkyl chains in monolayers.

[24] (a) Snyder, R. G.; Strauss, H. L.; Elliger, C. A. *J. Phys. Chem.* **1982**, *86*, 5145−5150. (b) Snyder, R. G.; Maroncelli, M.; Strauss, H. L.; Hallmark, V. M. *J. Phys. Chem.* **1986**, *90*, 5623−5630.

[25] The number of alkyl chains bonded through acyloxy linkages was estimated by dividing the ratio of the intensity of the C=O stretch and asymmetric methylene stretch in the monolayer spectrum by the ratio of areas of the carbonyl stretch and asymmetric methylene stretch in a Langmuir-Blodgett film of stearic acid on an oxidized silicon ATR plate.[26]

[26] Davies, G. H.; Yarwood, J. *Spectrochim. Acta* **1987**, *43A*, 1619−1923.

[27] Linford and Chidsey postulated[1] that hydrogens bonded to the H−Si(111) surface are replaced by bonds to adsorbate or to −OH groups as indicated by an increase in monolayer IR absorbance spectra from 3000 to 3700 cm^{-1}. The disappearance of the Si−H stretch also occurs with olefin-derived monolayers although in these cases a small peak in the Si−H stretching region (0.001−0.002 absorbance units) sometimes remains.

[28] Angst, D. L. Ph.D. Thesis, Lehigh University, Nov. 1991.

Table 1. Thickness, Infrared Absorption, and Wetting Properties of Monolayers

reactants[a]	d_{ellips} (Å)[b]	$\nu_a^{\text{p-pol}}$ (cm^{-1})[c]	$A_a^{\text{p-pol}}$[d]	$\theta_{a/r}(H_2O)$[e]	$\theta_{a/r}$(HD)[e]
100% $[C_{17}H_{35}C(O)O]_2$	25	2917.6	0.101	113°/95°	45°/43°
100% $C_{16}H_{33}CH{=}CH_2$	10	2923.5	0.034	108°/96°	47°/46°
100% $C_{16}H_{33}CH{=}CH_2$(150 °C)	17	2921.0	0.059	113°/105°	45°/42°
100% $C_{16}H_{33}CH{=}CH_2$ (200 °C)	18	2920.6	0.066	113°/110°	44°/43°
50% $[C_{17}H_{35}C(O)O]_2$/50% $C_{16}H_{33}CH{=}CH_2$	23	2917.7	0.104	111°/101°	48°/46°
10% $[C_{17}H_{35}C(O)O]_2$/90% $C_{16}H_{33}CH{=}CH_2$	20	2918.2	0.097	111°/100°	48°/47°
10% $[C_{17}D_{35}C(O)O]_2$/90% $C_{16}H_{33}CH{=}CH_2$	21	2918.5	0.087	112°/103°	48°/46°
5% $[C_{17}H_{35}C(O)O]_2$/95% $C_{16}H_{33}CH{=}CH_2$	21	2918.7	0.090	112°/97°	47°/47°
5% $[C_{17}D_{35}C(O)O]_2$/95% $C_{16}H_{33}CH{=}CH_2$	21	2919.1	0.078	113°/104°	45°/44°
100% $[C_{11}H_{23}C(O)O]_2$	17	2921.0	0.041	110°/96°	32°/18°
$C_{10}H_{21}CH{=}CH_2$	7	2923.6	0.020	103°/95°	13°/<10°
$C_{10}H_{21}CH{=}CH_2$ (150 °C)	12	2922.0	0.035	111°/104°	35°/34°
$C_{10}H_{21}CH{=}CH_2$ (200 °C)	13	2921.2	0.039	112°/107°	35°/34°
50% $[C_{11}H_{23}C(O)O]_2$/50% $C_9H_{19}CH{=}CH_2$	14	2920.0	0.042	112°/102°	47°/44°
50% $[C_{15}H_{31}C(O)O]_2$/50% $C_{14}H_{29}C{\equiv}CH$	26	2918.1	0.085	113°/108°	48°/46°
50% $[C_{11}H_{23}C(O)O]_2$/50% $C_{11}H_{23}C{\equiv}N$	11	2923.5	0.028	110°/100°	27°/25°
$C_{18}H_{37}SiCl_3$/oxidized Si (20 °C)	25	2917.6	0.117	112°/109°	47°/45°
$C_{12}H_{25}SiCl_3$/oxidized Si (20 °C)	17	2921.7	0.048	114°/112°	42°/39°
$C_{18}H_{37}SH$/Au (20 °C)	28	2917.9		114°/99°	50°/41°
$C_{12}H_{25}SH$/Au (20 °C)	17	2919.2		114°/104°	47°/39°

[a] All substrates were H−Si(111) heated to 100 °C for 1 h unless specified. Each data set is from a single representative surface. See the Experimental Section for sample-to-sample errors. [b] d_{ellips}: ellipsometric thickness. [c] $\nu_a^{\text{p-pol}}$: peak position of asymmetric methylene stretch observed with p-polarized light at an internal angle of incidence of 45°. [d] $A_a^{\text{p-pol}}$: Absorbance of asymmetric methylene stretch on 50 mm long × 1 mm thick ATR plates. [e] $\theta_{a/r}$: advancing and receding contact angles for H_2O and hexadecane (HD).

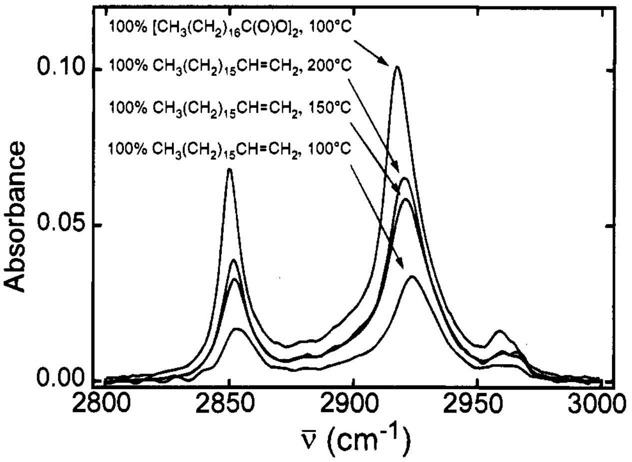

Figure 2. C−H infrared stretching region (p-polarized) of monolayers prepared from 100% $CH_3(CH_2)_{15}CH{=}CH_2$, at 200, 150, and 100 °C and from 100% $[CH_3(CH_2)_{16}C(O)O]_2$ at 100°C.

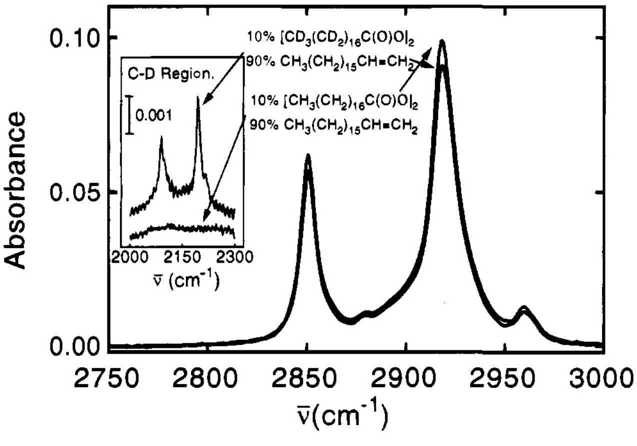

Figure 3. C−H and C−D stretching regions (p-polarized) of monolayers prepared from 10% $[CD_3(CD_2)_{16}C(O)O]_2$ and 90% $CH_3(CH_2)_{15}$-$CH{=}CH_2$ and from 10% $[CH_3(CH_2)_{16}C(O)O]_2$ and 90% $CH_3(CH_2)_{15}$-$CH{=}CH_2$.

and 10% $[CH_3(CH_2)_{16}C(O)O]_2$ and monolayers formed from 90% $CH_3(CH_2)_{15}CH{=}CH_2$ and 10% $[CD_3(CD_2)_{16}C(O)O]_2$. The intensity of the CH modes decreases by only about 10% on deuteration of the diacyl peroxide. That decrease is well matched by the appearance of corresponding CD_2 modes, the intensities of which account for about 10% of the monolayer after correction for the decreased oscillator strength of the C−D bonds.[29] The data collected in Table 1 indicate that about 90% of the monolayers are derived from the olefin, independent of whether 5% or 10% diacyl peroxide is used as initiator. Moreover, it is clear that the diacyl peroxide induces a higher coverage of the olefin than that obtained from the neat olefin.

Reaction of H−Si(111) with Other Olefins and Unsaturated Compounds. In order to explore the generality of the diacyl peroxide-activated adsorption of an unsaturated compound to the silicon surface, a series of experiments were performed involving shorter chain-length olefins, a chlorine-terminated olefin, and other unsaturated compounds.

As expected, a mixture of an olefin and a diacyl peroxide each containing less than 18 carbon atoms, such as 50% $CH_3(CH_2)_8CH{=}CH_2$ and 50% $[CH_3(CH_2)_{10}C(O)O]_2$, forms good monolayers with high water and hexadecane contact angles (see Table 1). In comparison to monolayers prepared from 100% $[CH_3(CH_2)_{10}C(O)O]_2$ on H−Si(111) or $C_{12}H_{25}SiCl_3$ on oxidized silicon, this monolayer is 3 Å thinner by ellipsometry but more solid-like by IR spectroscopy.

Monolayers have also been prepared from shorter-chain neat olefins. When H−Si(111) is heated to 100 °C for 1 h in the presence of 1-dodecene, a thin, liquid-like monolayer is formed (see Table 1). However, at 200 °C, a monolayer that compares quite favorably to that made from 50% $CH_3(CH_2)_8CH{=}CH_2$ and 50% $[CH_3(CH_2)_{10}C(O)O]_2$ is formed (see Table 1). Unlike the relative constancy of reactivity with chain length in the diacyl peroxide-induced reaction, the difference between the well-formed films made at 200 °C from 1-dodecene and the partial monolayers made at 200 °C from 1-octadecene suggests a substantial chain-length dependence in this chemistry.

In order to provide a label for the olefin and to explore the chemistry of olefins containing other functional groups, we heated H−Si(111) with 50% $Cl(CH_2)_9CH{=}CH_2$ and 50% $[CH_3$-$(CH_2)_{10}C(O)O]_2$. This film had an ellipsometric thickness of

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(29) The CD_2 oscillator strength is less than that of the CH_2 oscillator. To quantify this difference, the intensities of the asymmetric methylene stretches of octadecanethiol and perdeuterated hexadecanethiol on gold were divided by 17 and 15, respectively. These numbers were then ratioed to obtain a value of 2.74. The monolayer substrates were freshly prepared ~2000 Å Au films on ~150 Å Ti on silicon wafers.

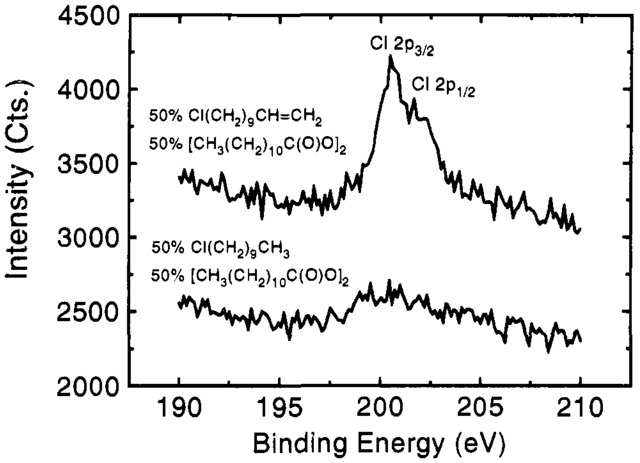

Figure 4. Cl 2p region of X-ray photoelectron spectra of monolayers prepared from 50% $Cl(CH_2)_9CH{=}CH_2$ and 50% $[CH_3(CH_2)_{10}C(O)O]_2$ and from $Cl(CH_2)_9CH_3$ and 50% $[CH_3(CH_2)_{10}C(O)O]_2$.

14 Å and a relatively low contact angle of 99°, which suggests chlorine termination of the monolayer. Conclusive evidence for chlorine incorporation in the film is provided by X-ray photoelectron spectroscopy as shown in Figure 4. Comparison of the Cl 2p and C 1s intensities for this monolayer shows that about 90% of its carbon chains are terminated with chlorine. This result, along with the high incorporation of olefin seen in the deuterium-labeling experiment, leads us to the conclusion that a roughly constant fraction (~90%) of the chains are derived from the olefin.

Because it is known that molecular silicon hydrides can behave as reducing agents under free radical conditions,[4,30] it was necessary to perform a control experiment to ensure that the monolayer was formed predominantly by olefin adsorption and not by chlorination of the silicon surface accompanied by diacyl peroxide adsorption. A mixture of 50% $Cl(CH_2)_9CH_3$ and 50% $[CH_3(CH_2)_{10}C(O)O]_2$ was used in the control experiment.[31] As shown in Figure 4, relatively little chlorine is incorporated under these conditions. The advancing water contact angle for the control surface is 103° which is somewhat higher than that for the surface formed from 50% $Cl(CH_2)_9CH{=}CH_2$ and 50% $[CH_3(CH_2)_{10}C(O)O]_2$ as expected if reaction with the diacyl peroxide predominates. These results demonstrate that the olefin chemistry is compatible with chlorine termination, which makes subsequent terminal-group derivitization of these monolayers possible.[32]

It is of interest to ascertain whether olefins are the only class of unsaturated molecules capable of binding to the silicon surface under diacyl peroxide initiation. We found that mixtures of 1-alkynes and diacyl peroxides can be used to prepare monolayers of similar quality to those made from mixtures of olefins and diacyl peroxides[33] (see Table 1). However, under the same conditions, a mixture of 50% $CH_3(CH_2)_{10}C{\equiv}N$ and 50% $[CH_3(CH_2)_{10}C(O)O]_2$ did not form nearly as dense a monolayer as the mixture of 50% $CH_3(CH_2)_8CH{=}CH_2$ and 50% $[CH_3(CH_2)_{10}C(O)O]_2$ (see Table 1).

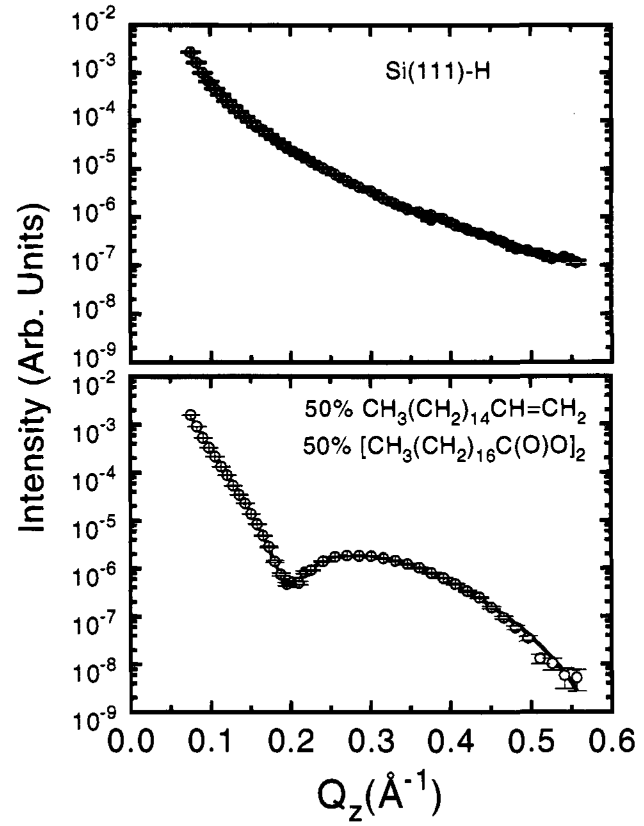

Figure 5. X-ray reflectivity of a bare H−Si(111) and of a monolayer prepared from 50% $CH_3(CH_2)_{14}CH{=}CH_2$ and 50% $[CH_3(CH_2)_{16}C(O)O]_2$. Error bars are shown and solid lines are the fits to the data sets.

X-ray Reflectivity. To characterize more fully the monolayers prepared in this work, we measured the X-ray reflectivity of some of the films. This technique provides a determination of the film thickness which is less model dependent than ellipsometry. Figure 5 shows X-ray reflectivity as a function of momentum transfer, Q_z, for both an unmodified hydrogen-terminated silicon surface and a sample prepared from 50% $CH_3(CH_2)_{14}CH{=}CH_2$ and 50% $[CH_3(CH_2)_{16}C(O)O]_2$.

At grazing incidence, the reflectivity of a flat surface is high but rapidly decreases as the angle between the surface and incident X-ray beam is increased. Unlike the smooth Fresnel-like decay of the H−Si(111) surface, the sample prepared from 50% $CH_3(CH_2)_{14}CH{=}CH_2$ and 50% $[CH_3(CH_2)_{16}C(O)O]_2$ shows a clear interference minimum at which the reflectivity decreases by about 1.5 orders relative to the H−Si(111) surface. Pomerantz and co-workers observed a similar minimum for octadecyltrichlorosilane monolayers on oxidized silicon.[21] This dip at roughly 0.2 $Å^{-1}$ ($2\theta = 1.4°$) is due to destructive interference between X-ray scattered at two interfaces separated by approximately 16 Å. By fitting the reflectivity data to a standard formalism, we find a thickness of 16.0 ± 0.1 Å and an electron density of $\varrho_{ml} = 0.30 \pm 0.02$ $e^-/Å^3$ (87% the density of crystalline $C_{33}H_{68}$[34]). Because of the limited data range, the monolayer and substrate roughnesses, σ_{ml} and σ_o, respectively, are indistinguishable in the analysis and values of these roughnesses at 3.1 ± 0.5 Å result in acceptable fits. The hydrogen-terminated silicon surface has a roughness of 2.6 ± 0.5 Å and so the values of σ_{ml} and σ_o suggest a small roughening

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(30) Ballestri, M.; Chatgilialoglu, C.; Guerra, M.; Guerrini, A.; Lucarini, M.; Seconi, G. *J. Chem. Soc., Perkin Trans. 2* **1993**, *3*, 421−425.

(31) Physical properties for the control monolayer prepared from 50% $Cl(CH_2)_9CH_3$ and 50% $[CH_3(CH_2)_{10}C(O)O]_2$ are the following: d_{ellips} = 11 Å, $\theta_{a/r}(H_2O)$ = 103°/84°, $\theta_{a/r}(HD) < 10°$ (wet by HD).

(32) Under the same experimental conditions, 50% ω-bromo-1-undecene/50% $[CH_3(CH_2)_{10}C(O)O]_2$ yielded a partial, poorly organized monolayer.

(33) A small peak at 1600.8 cm^{-1} (0.0044 absorbance units) in the spectrum of the monolayer prepared from 50% $CH_3(CH_2)_{13}C{\equiv}CH$ and 50% $[CH_3(CH_2)_{14}C(O)O]_2$ suggests a carbon-carbon double bond in the film as expected for the hydrosilylation of an alkyne. However, no peaks are observed in the IR C−H stretching region above 3000 cm^{-1}. A methyl-terminated monolayer could also be prepared from a mixture of 50% $CH_3(CH_2)_9C{\equiv}CH$ and 50% $[CH_3(CH_2)_{10}C(O)O]_2$: d_{ellips} = 16 Å, $\theta_{a/r}(H_2O)$ = 111°/102°, $\theta_{a/r}(HD)$ = 47°/45°.

(34) Ewen, B.; Strobl, G. R.; Richter, D. *Faraday Discuss. Chem. Soc.* **1980**, *69*, 19.

Table 2. Infrared Dichroism of Monolayers from 18-Carbon Precursors

	asymmetric stretch			symmetric stretch			orientation		
reactants[a]	$\nu_a^{s\text{-pol}}$ (cm^{-1}) $\nu_a^{p\text{-pol}}$ (cm^{-1})	$A_a^{s\text{-pol}}$ $A_a^{p\text{-pol}}$	α_a[c]	$\nu_s^{s\text{-pol}}$ (cm^{-1}) $\nu_s^{p\text{-pol}}$ (cm^{-1})	$A_s^{s\text{-pol}}$ $A_s^{p\text{-pol}}$	α_s[c]	θ[d]	γ[e]	d_{ellips}[b] (Å)
100% $[C_{17}H_{35}C(O)O]_2$	2917.5	0.107	74°	2850.0	0.073	76°	22°	49°	25
	2917.6	0.101		2850.1	0.069				
100% $C_{16}H_{33}CH{=}CH_2$	2923.1	0.029	51°	2853.4	0.015	55°	58°	48°	10
	2923.5	0.034		2852.6	0.017				
100% $C_{16}H_{33}CH{=}CH_2$ (150 °C)	2920.5	0.060	68°	2851.8	0.033	66°	34°	43°	17
	2921.0	0.059		2852.0	0.033				
100% $C_{16}H_{33}CH{=}CH_2$ (200 °C)	2921.2	0.067	67°	2851.1	0.039	64°	36°	42°	18
	2920.6	0.066		2851.6	0.040				
50% $[C_{17}H_{35}C(O)O]_2$/50% $C_{16}H_{33}CH{=}CH_2$	2917.7	0.107	69°	2850.2	0.070	72°	28°	49°	23
	2917.7	0.104		2850.2	0.067				
10% $[C_{17}H_{35}C(O)O]_2$/90% $C_{16}H_{33}CH{=}CH_2$	2918.4	0.099	69°	2850.6	0.063	64°	34°	39°	20
	2918.2	0.097		2850.3	0.063				
10% $[C_{17}D_{35}C(O)O]_2$/90% $C_{16}H_{33}CH{=}CH_2$	2918.5	0.091	73°	2850.6	0.057	68°	28°	38°	21
	2918.5	0.087		2850.7	0.056				
5% $[C_{17}H_{35}C(O)O]_2$/95% $C_{16}H_{33}CH{=}CH_2$	2918.6	0.093	70°	2850.8	0.058	65°	33°	39°	21
	2918.7	0.090		2850.8	0.058				
5% $[C_{17}D_{35}C(O)O]_2$/95% $C_{16}H_{33}CH{=}CH_2$	2919.1	0.079	68°	2851.0	0.049	67°	33°	44°	21
	2919.1	0.078		2851.1	0.048				
$C_{18}H_{37}SiCl_3$/oxidized Si (20 °C)	2917.4	0.126	79°	2850.1	0.085	82°	14°	54°	25
	2917.6	0.117		2850.1	0.078				

[a] All substrates were H−Si(111) heated to 100 °C for 1 h unless specified. [b] The thickness is repeated from Table 1. [c] α: angle between the surface normal and the symmetric or asymmetric CH_2 transition dipole moment. [d] θ: average tilt angle of the alkyl chain from the surface normal. [e] γ: twist angle of the average plane of the carbon atoms in the chain with respect to the plane of tilt.

of the substrate upon monolayer formation. Similar results were obtained for other films.

The film thickness of 16 Å found by X-ray reflectivity is significantly less than the value we determined for this surface by optical ellipsometry (20 Å). However, Wasserman and coworkers[20] have similarly observed that thicknesses of alkylsiloxane monolayers on oxidized silicon determined by X-ray reflectivity are consistently lower than those found by optical ellipsometry, though in their case by only about 2 Å. Because refractive indices at X-ray wavelengths are only slightly different than unity,[20] the thickness measured by X-ray reflectivity is essentially independent of the density of the film. Moreover, the X-ray probe has a wavelength comparable to the monolayer thickness making the measurement intrinsically very precise. In contrast, the absolute thickness measured by optical ellipsometry should be interpreted with care since it depends on the extrapolation of bulk optical properties to distances that are small relative to the wavelength of the scattered radiation.

IR Dichroism. By comparing the IR stretching-mode intensities obtained using p- and s-polarized light, and assuming the chains to be in the all-trans conformation, one can obtain information about the tilt of alkyl chains from the surface normal and the twist of the average plane of the carbon atoms in the chain with respect to the plane of tilt (see Experimental Section). Although the angles determined by dichroism turn out to be relatively imprecise (see Experimental Section), they do provide complementary information that supplements that obtained from the individual IR absorption spectra and the X-ray reflectivity measurements. Table 2 presents the p- and s-polarized intensities and transition dipole moment angles, α, of the methylene stretching modes, chain tilt angles, θ, chain twist angles, γ, and ellipsometric thicknesses of monolayers prepared from 18-carbon precursors on silicon and oxidized silicon. A chain tilt angle of approximately 30° is found for monolayers prepared from mixtures of olefins and diacyl peroxides. This value is quite similar to that of analogous chain length thiols on gold.[13] We observe that for greater tilt angles the films are consistently less thick. The calculated chain twist angles, γ, for all the surfaces in Table 2 are near 45°, which is close to values reported for thiols on gold (~55°)[35] and GaAs (45 ± 5°).[3b]

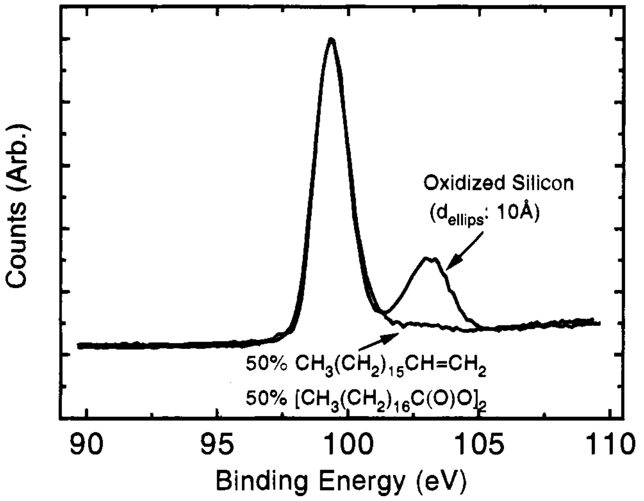

Figure 6. Si 2p region of the X-ray photoelectron spectrum of a monolayer prepared from 50% $CH_3(CH_2)_{15}CH{=}CH_2$ and 50% $[CH_3(CH_2)_{16}C(O)O]_2$ and subsequently exposed to boiling $CHCl_3$ (2 h), boiling H_2O (7 h), and air (11 weeks). A normalized spectrum of a silicon shard with 10 Å of oxide is shown for comparison. (Each spectrum has been shifted slightly to bring the bulk Si 2p peak to the known bulk Si 2p value.)

Inhibition of Silicon Oxidation. For any application of monolayers on silicon that requires protection or passivation of the underlying silicon, the oxidation of the silicon substrate is an issue. We find that these surfaces, like the H−Si(111) surface, are quite stable to air oxidation. Figure 6 shows the normalized XPS Si 2p spectrum of a monolayer prepared from 50% $CH_3(CH_2)_{15}CH{=}CH_2$ and 50% $[CH_3(CH_2)_{16}C(O)O]_2$ on H−Si(111) which was exposed to hot solvents (2 h in boiling $CHCl_3$ and 7 h in boiling water) followed by exposure to the air for 11 weeks. Of particular significance is the near absence of oxidized silicon as evidenced by the lack of signal in the

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(35) Nuzzo, R. G.; Dubois, L. H.; Allara, D. L. *J. Am. Chem. Soc.* **1990**, *112*, 558−569.

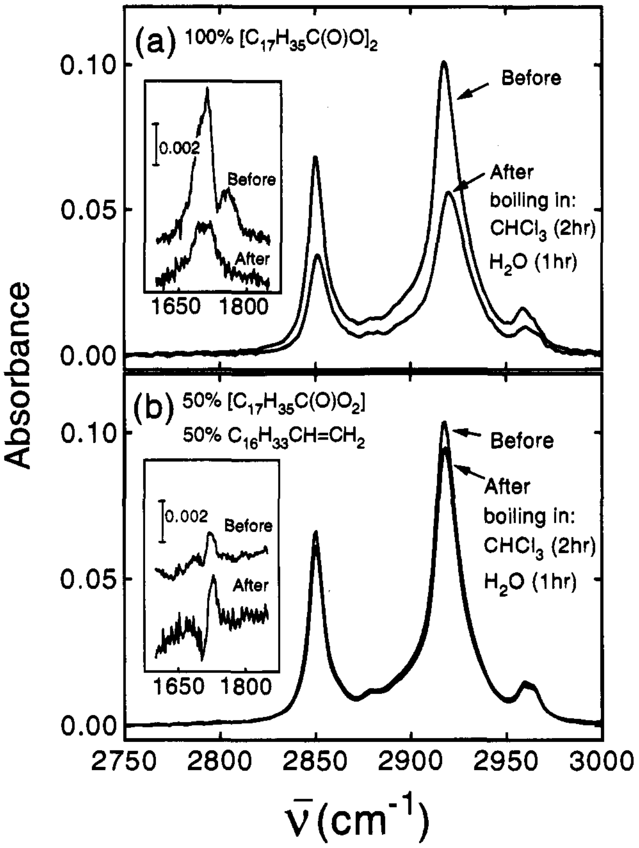

Figure 7. C–H and carbonyl stretching regions (p-polarized) of monolayers prepared from (a) 100% $[CH_3(CH_2)_{16}C(O)O]_2$ and (b) 50% $CH_3(CH_2)_{15}CH{=}CH_2$ and 50% $[CH_3(CH_2)_{16}C(O)O]_2$ shown before and after exposure to boiling $CHCl_3$ (2 h) and boiling H_2O(1 h).

region around 103.5 eV. The normalized spectrum of a shard of clean silicon with 10 Å of superficial oxide is shown for comparison. Equal or lesser quantities of oxidized silicon were also observed on surfaces made from 50% $CH_3(CH_2)_{13}CH{=}CH_2$ and 50% $[CH_3(CH_2)_{14}C(O)O]_2$ and from 100% $[CH_3(CH_2)_{10}C(O)O]_2$ that were exposed to the air for 35 and 33 days, respectively. This result shows that neither the reagents used for monolayer preparation, nor the stability tests, nor the presence of the monolayer on the surface over time induce significant oxidation of the silicon substrate.

Stability Tests. We have performed monolayer stability tests under a wide variety of conditions which include hot organic solvent, hot water, fluoride, hot acid, and hot base. Figure 7 compares the effects of exposing monolayers made from 100% $[CH_3(CH_2)_{16}C(O)O]_2$ (Figure 7a) and from 50% $CH_3(CH_2)_{15}CH{=}CH_2$ and 50% $[CH_3(CH_2)_{16}C(O)O]_2$ (Figure 7b) to boiling chloroform for 2 h followed by boiling water for 1 h. The loss of intensity shown in both the C–H stretching region and, to a greater extent, in the carbonyl region of the spectrum for the monolayer formed from the neat diacyl peroxide has been discussed previously[1] and was attributed to the presence of a significant number of alkyl chains bound through a hydrolyzable Si–OC(O)- linkage.[36]

The poor stability of the monolayer formed from 100% $[CH_3(CH_2)_{16}C(O)O]_2$ in Figure 7a is contrasted to the much greater stability of the monolayer formed from 50% $CH_3(CH_2)_{15}CH{=}CH_2$ and 50% $[CH_3(CH_2)_{16}C(O)O]_2$ (Figure 7b). After similar exposure to boiling chloroform and boiling water, only a small decrease is observed in the intensity of the C–H stretching region of this monolayer. We ascribe the increased hydrolytic stability of the monolayer shown in Figure 7b to a decreased number of alkyl chains bound through hydrolyzable acyloxy linkages. This interpretation is substantiated by the difference in carbonyl absorption between the spectra for the two monolayers (compare insets of Figures 7a and 7b).

Table 3 shows the results of similar stability tests with a large set of monolayers on silicon and, for comparison, with monolayers of octadecyltrichlorosilane on oxidized silicon and octadecanethiol on gold. The comparison tests were performed because of the reported "remarkable physical and chemical stability"[21] of the silane monolayers and the extensive current interest in thiol monolayers. As expected from the previous discussion of Figure 7, Table 3 shows that monolayers prepared from neat diacyl peroxide are easily damaged in these stability tests. The thicknesses, absorptions, and contact angles of these monolayers decrease while the frequencies of the asymmetric methylene stretches increase. In contrast, monolayers prepared from mixtures of olefins and diacyl peroxides and from neat, heated olefins are not strongly affected by the boiling solvents. Note also that the octadecyltrichlorosilane monolayer is quite stable to boiling solvents, whereas the octadecanethiol monolayer is substantially damaged after only 30 min in boiling chloroform. After the stability tests, measurement of the IR dichroism (not shown) for the monolayers formed from neat diacyl peroxide indicated that the tilt angle of the chains had increased from 22° to 33°. No similar increase in tilt angle was observed for olefin-derived monolayers.

Additional stability tests were performed to evaluate the resistance of the monolayers to fluoride, acidic, and basic solutions. Monolayers formed from 90% $CH_3(CH_2)_{15}CH{=}CH_2$ and 10% $[CH_3(CH_2)_{16}C(O)O]_2$ and from $C_{18}H_{37}SiCl_3$ on oxidized silicon were tested for stability to fluoride by immersion in 48% aqueous HF. This reagent was chosen because it attacks silicon–oxygen bonds such as those present in silane-derived monolayers but does not as readily cleave silicon–carbon bonds. After a 1 h immersion in this reagent, the thickness of the olefin-derived monolayer increased slightly from 21 to 23 Å, while its wetting properties remained constant. Conversely, the silane-derived monolayer decreased in thickness from 26 to 16 Å. Its wetting properties were also affected, as shown by decreases in the contact angles: from $\theta_{a/r}(H_2O)$ = 113°/110° and $\theta_{a/r}$(HD) = 47°/47° to 104°/84° and 34°/24°, respectively. Thus the olefin-derived monolayers are observed to be more stable to fluoride than the silane-derived monolayers, suggesting that silicon–oxygen bonding is not responsible for the stability of the olefin-derived monolayers.

Table 4 shows the stability of monolayers prepared from 50% $CH_3(CH_2)_{15}CH{=}CH_2$ and 50% $[CH_3(CH_2)_{16}C(O)O]_2$ and from $C_{18}H_{37}SiCl_3$ on oxidized silicon to boiling 10% aqueous 1 M NH_4OH or 2.5 M H_2SO_4 in 90% dioxane by volume.[37,38] Dioxane was used to ensure that organic material from the monolayer would be soluble in the test medium. The physical properties of the monolayers prepared from 50% $CH_3(CH_2)_{15}CH{=}CH_2$ and 50% $[CH_3(CH_2)_{16}C(O)O]_2$ were not altered significantly by these tests. In contrast, monolayers made from $C_{18}H_{37}SiCl_3$ on oxidized silicon decreased in thickness by about 5 Å while their wetting properties remained virtually constant. Both films were badly damaged and the surfaces left visibly

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(36) The asymmetric methylene stretch shown in Figure 7a decreases in area (full width at half height × height) by 33% after the solvent stability tests.

(37) Refluxing mixtures of dioxane and concentrated aqueous HCl are typically used in the purification of this solvent.[38] Therefore dioxane (a cyclic ether) should not be cleaved to any significant degree under the acidic conditions described in this work.

(38) Fieser, L. F.; Fieser, M. *Reagents for Organic Synthesis*; Wiley: New York, 1967; Vol. 1, p 333.

Table 3. Physical Properties of Monolayers Before and After Solvent Stability Tests

reactants	stability test	d_{ellips} (Å)	$\nu_a^{p\text{-}pol}$	$A_a^{p\text{-}pol}$	$\theta_{a/r}(H_2O)$	$\theta_{a/r}$(HD)
100% $[C_{17}H_{35}C(O)O]_2$	initial	25	2917.6	0.101	113°/95°	45°/43°
	2 h $CHCl_3$ (61 °C)	21	2918.3	0.077	112°/106	47°/43°
	+ 1 h H_2O (100 °C)	18	2920.0	0.056	108°/103°	45°/42°
100% $C_{16}H_{33}CH{=}CH_2$	initial	10	2923.5	0.034	108°/96°	47°/46°
	2 h $CHCl_3$ (61° C)	11	2924.8	0.033	107°/98°	43°/40°
	+1 h H_2O (100 °C)	14	2924.7	0.032	98°/82°	36°/31°
100% $C_{16}H_{33}CH{=}CH_2$ (150 °C)	initial	17	2921.0	0.059	113°/105°	45°/42°
	2 h $CHCl_3$ (61 °C)	18	2922.1	0.061	113°/107°	44°/43°
	+1 h H_2O (100 °C)	18	2921.4	0.058	112°/107°	43°/42°
100% $C_{16}H_{33}CH{=}CH_2$ (200 °C)	initial	18	2920.6	0.066	113°/110°	44°/43°
	3 h $CHCl_3$ (61° C)	18	2920.6	0.065	113°/108°	45°/43°
	+1 h H_2O (100 °C)	19	2921.3	0.061	113°/108°	43°/41°
100% $C_{10}H_{21}CH{=}CH_2$ (150 °C)	initial	12	2922.0	0.035	111°/104°	35°/34°
	2 h $CHCl_3$ (61 °C)	13	2922.1	0.035	109°/103°	36°/35°
	+1 h H_2O (100 °C)	14	2921.9	0.032	108°/98°	33°/30°
100% $C_{10}H_{21}CH{=}CH_2$ (200 °C)	initial	13	2921.2	0.039	112°/107°	35°/34°
	2 h $CHCl_3$ (61 °C)	14	2921.0	0.036	111°/105°	33°/32°
	+1 h H_2O (100 °C)	14	2921.0	0.036	111°/106°	34°/31°
50% $[C_{17}H_{35}C(O)O]_2$/50% $C_{16}H_{33}CH{=}CH_2$	initial	23	2917.7	0.104	111°/101°	48°/46°
	2 h $CHCl_3$ (61 °C)	22	2918.1	0.096	111°/101°	48°/46°
	+1 h H_2O (100 °C)	23	2918.1	0.096	112°/104°	47°/46°
	+6 h H_2O (100 °C)	23	2918.2	0.091	112°/106°	48°/46°
50% $[C_{17}D_{35}C(O)O]_2$/95% $C_{16}H_{33}CH{=}CH_2$	initial	21	2919.1	0.078	113°/104°	45°/44°
	2 h $CHCl_3$ (61 °C)	21	2919.4	0.075	112°/99°	45°/43°
	+1 h H_2O (100 °C)	20	2919.6	0.072	112°/107°	46°/44°
50% $[C_{11}H_{23}C(O)O]_2$/50% $C_9H_{19}CH{=}CH_2$	initial	14	2920.0	0.042	112°/102°	47°/44°
	2 h $CHCl_3$ (61 °C)	14	2920.3	0.040	112°/103°	46°/43°
	+1 h H_2O (100 °C)	13	2920.2	0.039	112°/103°	46°/43°
50% $[C_{15}H_{31}C(O)O]_2$/50% $C_{14}H_{29}C{\equiv}CH$	initial	26	2918.1	0.085	113°/108°	48°/46°
	2 h $CHCl_3$ (61 °C)	25	2918.2	0.082	113°/101°	48°/47°
	+1 h H_2O (100 °C)	21	2918.6	0.074	113°/107°	48°/47°
	+6 h H_2O (100 °C)	22	2919.4	0.062	112°/99°	47°/45°
50% $[C_{11}H_{23}C(O)O]_2$ /50% $C_{11}H_{23}C{\equiv}N$	initial	11	2923.5	0.028	110°/100°	27°/25°
	2 h $CHCl_3$ (61 °C)	11	2926.0	0.013	91°/78°	<10°
$C_{18}H_{37}SiCl_3$/oxidized Si (20 °C)	initial	25	2917.6	0.117	112°/109°	47°/45°
	2 h $CHCl_3$ (61 °C)	24	2918.5	0.092	114°/110°	46°/44°
	+1 h H_2O (100 °C)	23	2919.1	0.084	113°/102°	45°/43°
$C_{18}H_{37}SH$/Au (20 °C)	initial	28	2917.9	0.0054	114°/99°	50°/41°
	0.5 h $CHCl_3$ (61 °C)	20	2920.8	0.0062	112°/101°	47°/37°

Table 4. Thickness and Wetting Properties of Monolayers After Acid and Base Stability Tests

reactants	stability test	d_{ellips} (Å)	$\theta_{a/r}(H_2O)$	$\theta_{a/r}$(HD)
50% $[C_{17}H_{35}C(O)O]_2$/50% $C_{16}H_{33}CH{=}CH_2$	initial	22	114°	47°
	1 h aqueous 10% 1 M NH_4OH/90% dioxane (boiling)	21	114°	46°
$C_{18}H_{37}SiCl_3$/oxidized Si (20 °C)	initial	27	114°	47°
	1 h aqueous 10% 1 M NH_4OH/90% dioxane (boiling)	21	111°	45°
50% $[C_{17}H_{35}C(O)O]_2$/50% $C_{16}H_{33}CH{=}CH_2$	initial	22	113°	47°
	1 h aqueous 10% 2.5 M $H_2SO_4$90% dioxane (boiling)	22	112°	47°
$C_{18}H_{37}SiCl_3$/oxidized Si (20 °C)	initial	25	113°	48°
	1 h aqueous 10% 2.5 M H_2SO_4 90% dioxane (boiling)	21	112°	46°

pitted and etched by 1 h in boiling 90% dioxane/10% aqueous 1 M NaOH.[39]

Discussion

Monolayer Composition. The data we have presented above suggest that the majority of the films discussed in this work are methyl-terminated monolayers of densely-packed alkyl chains. Methyl termination of the monolayers is indicated by their high water and hexadecane contact angles, which are known to be indicative of methyl termination.[12] That the films are monomolecular layers is suggested by their consistent thicknesses, which are approximately the lengths of the alkyl chains of which the films are comprised. The dense packing of the alkyl chains is shown by the frequencies of the asymmetric methylene stretching modes in the infrared absorption spectra and also by the electron density found by X-ray reflectivity. These features are similar to those known for the self-assembled monolayers of trichloroalkylsilanes on oxidized silicon and alkanethiols on gold.[13,17]

The high stability of the olefin-derived monolayers in boiling solvents and boiling aqueous solutions suggests chemisorption, and not physisorption, of the monolayer to the substrate, and delineates more clearly the conditions under which these films could be used in future applications. Moreover, these monolayers are more stable than the trichloroalkylsilane-derived monolayers to fluoride, suggesting that the bonding between the monolayer and the substrate is not due to Si−O bonds.

Deuterium labeling of the diacyl peroxide used to initiate monolayer formation with olefins shows that the majority of the alkyl chains in olefin-derived monolayers (~90%) comes from the olefin and not the diacyl peroxide. A monolayer prepared from a chlorine-terminated alkene and a diacyl peroxide is also primarily derived from the olefin.

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[39] 1 h in hot (85 °C) ~3:1 H_2SO_4(conc):H_2O_2 (30%) by volume also completely removes the monolayer but does not etch or pit the underlying silicon.

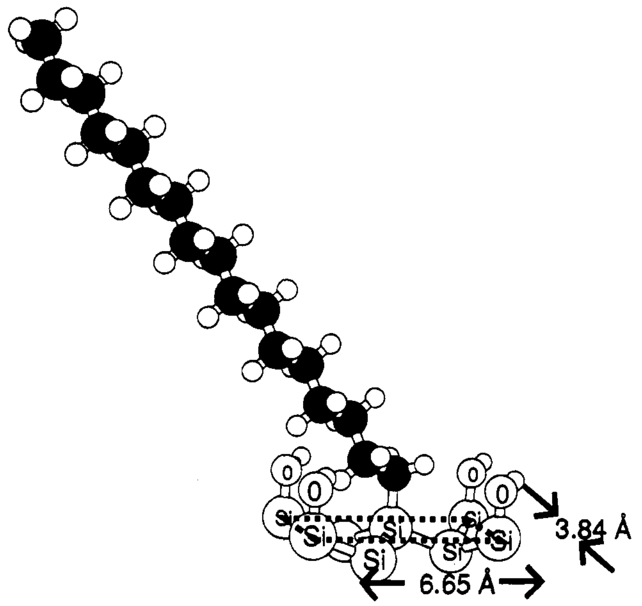

Figure 8. Hypothetical model of a unit cell containing one alkyl chain and one hydroxyl group alternatively bonded to Si(111) in a (2 × 1) overlayer structure.

Structure of the Olefin-Derived Monolayers. Based on the above results, we hypothesize that the majority of the chains in the olefin-derived monolayers are connected to the silicon substrate by silicon−carbon bonds. We also hypothesize that surface silicon atoms not terminated by chains are terminated by −OH groups, as suggested by infrared spectroscopy. By analogy with related molecular organosilicon compounds, such a monolayer should be stable to organic solvents and to hydrolytic conditions at ambient and moderately elevated temperatures. Before discussing a possible mechanism for the formation of this monolayer, we discuss a heuristic model for its structure.

A hypothetical unit cell containing one alkyl chain and one hydroxyl group covalently bound to a Si(111) surface is shown in Figure 8. The area of the unit cell is 25.5 Å^2, significantly greater than the minimum area needed for an alkyl chain (18.5 Å^2 in crystalline n-$C_{33}H_{68}$[34]). If all the carbon−carbon bonds in the chain were in the most stable trans geometry, the chain axis would be tilted 35° from the surface normal, the film thickness would be 18.3 Å,[40] and the chain twist (γ) would be 0° between the plane of carbon atoms and the plane of tilt. These values do not agree with the film thickness measured by X-ray reflectivity nor with the chain twist angle measured by IR dichroism. To account for the film thickness, we have shown the chain in Figure 8 rotated by 37° about the first carbon−carbon bond to obtain a thickness of 16.0 Å as measured by X-ray reflectivity. This gives a chain tilt (θ) of 45° and a chain twist (γ) of 53°,[40] in qualitative agreement with the very imprecise values of θ and γ that range from 28−36° and 40−50°, respectively, for the olefin-derived monolayers in Table 2.

The density of the chains in the hypothetical unit cell shown in Figure 8 would be approximately equal to that of crystalline paraffins such as n-$C_{33}H_{68}$.[34] Because the density measured by X-ray reflectivity for the olefin-derived monolayers is only about 90% of this value, we suspect that the real monolayers have a significant number of defects that account for this decreased density. Such defects, as well as acyloxy groups in the monolayer, may account for the observed increase in surface roughness on monolayer formation and may prevent the formation of a lattice with long-range periodicity. Diffraction or probe microscopy studies will be necessary to reveal the actual spacing of the chains on the surface. Electron and/or vibrational spectroscopy will be needed to convincingly demonstrate the presence of a silicon−carbon bond.

Mechanism of Monolayer Formation. In this section we propose a mechanism for the formation of the silicon−carbon bond suggested above and compare it to analogous homogeneous reactions that yield silicon−carbon bonds.

In previous work with neat diacyl peroxides, Linford and Chidsey[1] attributed the adsorption of alkyl chains derived from the diacyl peroxide to a series of free-radical reactions. They suggested that the peroxide bond first breaks homolytically to form two acyloxy radicals:

$$[RC(O)O_2]_2 \rightarrow 2RC(O)O\cdot \qquad (1)$$

Each of these may break apart to form an alkyl radical and carbon dioxide:

$$RC(O)O\cdot \rightarrow R\cdot + CO_2 \qquad (2)$$

Next, one of these two radical species, designated R′•, is proposed to abstract a hydrogen atom from the hydrogen-terminated silicon surface:

$$R'\cdot + HSi(111) \rightarrow R'H + \cdot Si(111) \qquad (3)$$

Finally, the resultant silicon dangling bond either couples with another radical or stimulates the decomposition of another diacyl peroxide molecule by coupling to one of its acyloxy fragments to give an acyloxy-bound surface chain.[41]

In the present case of the diacyl peroxide-induced reaction of an olefin with the hydrogen-terminated silicon surface, we propose that a related set of reactions occurs. The first steps are the same as eqs 1−3 above and result in hydrogen abstraction from the surface to leave a silicon dangling bond. We propose that this activation step is followed by addition of an olefin to the silicon dangling bond to form a surface-bonded, secondary carbon radical:

$$R''CH{=}CH_2 + \cdot Si(111) \rightarrow R''(CH\cdot)CH_2Si(111) \qquad (4)$$

This radical may then abstract another hydrogen from the allylic position of an unreacted olefin:

$$R''(CH\cdot)CH_2Si(111) + R''CH_2CH{=}CH_2 \rightarrow R''(CH_2)_2Si(111) + R''CH\cdot CH{=}CH_2 \qquad (5)$$

or from another Si−H group on the surface:

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[40] To find the angle (θ) between the surface normal (**n**) and the chain axis (**A**) as a function of rotation (β) about the first two carbon atoms, we used the formula $\theta = \cos^{-1}(\mathbf{n}\cdot\mathbf{A})$ where **n** and **A** are unit vectors. This can be shown to reduce to $\theta = \cos^{-1}[\sin\phi\cos(\phi/2)\cos\beta - \cos\phi\sin(\phi/2)]$ where ϕ is the C−C−C bond angle and we have assumed that the Si−C bond in Figure 8 is parallel to **n**. To find the angle of twist (γ), which is the angle between the plane of carbon atoms and the plane of tilt (the plane containing the chain axis and the surface normal) the following formula was used and evaluated numerically: $\gamma = \cos^{-1}\{[(\mathbf{c}\times\mathbf{A})\cdot(\mathbf{A}\times\mathbf{n})]/[|\mathbf{c}\times\mathbf{A}|\ |\mathbf{A}\times n|\ ]\}$, where **c** is the unit vector pointing along the first C−C bond, $\mathbf{c}\times\mathbf{A}$ is a vector perpendicular to the plane of carbon atoms, and $\mathbf{A}\times n$ is a vector perpendicular to the plane of tilt. The film thickness is found using $d_{\text{monolayer}} = 1.86\ \text{Å} + (1/2)(n-1)(2.52\ \text{Å})\cos\theta$, where 1.86 Å is the Si−C bond distance, n is the number of carbons in the alkyl chain, and 2.52 Å is the distance between next nearest carbons in a hydrocarbon chain.

[41] Kochi, J. K. *Free Radicals*; John Wiley: New York, 1973; pp 116−120.

$$R''(CH^{\bullet})CH_2Si(111) + HSi(111) \rightarrow R''(CH_2)_2Si(111) + {}^{\bullet}Si(111) \quad (6)$$

Both reactions 5 and 6 are energetically feasible and we cannot reasonably estimate which is likely to be most prevalent.

There is a strong analogy between the reactivity proposed here and that observed when olefins and small amounts of diacyl peroxides are heated with simple, small molecules containing the silicon–hydrogen bond[5] or when olefins and free-radical initiators are treated with polysilanes containing Si–H bonds.[42] For instance, trichlorosilane can be induced to add to 1-octene by heating with diacetylperoxide.[5] This reactivity was explained by a mechanism similar to that described above in which the diacetyl peroxide decomposes (analogous to eqs 1 and 2) and abstracts a hydrogen from trichlorosilane (analogous to eq 3). The resulting silicon radical adds to 1-octene (analogous to eq 4). The secondary radical created in this process can abstract a hydrogen from another trichlorosilane (analogous to eq 6). Similar reactions are also known for tris(trimethylsilyl)silane,[43,44] a small molecule that has the same bonding adjacent to the reactive Si–H bond as found on the H–Si(111) surface. In this case, the additions are known to be chain reactions that propagate for many cycles.[4] A propagating chain reaction may also occur in the formation of the olefin-derived monolayers. We plan to examine this possibility in future work.

Other modes of reaction seem less likely. In particular, radical-induced coupling of the olefins is known to not be an efficient process for olefins with allylic hydrogens because the allylic hydrogens are readily abstracted by the secondary radicals formed in eq 4.

Summary

Alkyl monolayers on silicon have been successfully formed by pyrolysis of mixtures of either 1-alkenes or 1-alkynes and diacyl peroxides. This new preparation of monolayers may be mechanistically similar to known radical-activated hydrosilylations of olefins. Experiments with deuterium-labeled peroxides and with ω-chloroalkenes demonstrate that the alkene and not the initiator binds primarily to the silicon surface. The resulting monolayers are densely packed, are tilted from the surface normal, inhibit oxidation of the underlying silicon substrate, and are shown to be at least as stable as similar chain length alkylsiloxane monolayers to hot solvents, acids, and bases and more stable than alkylsiloxane monolayers to HF.

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