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Alkyl Monolayers Covalently Bonded to Silicon Surfaces

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We have prepared densely packed alkyl monolayers covalently bound to Si(111) and Si(100) surfaces by the pyrolysis of diacyl peroxides ($[CH_3(CH_2)_nC(O)O]_2$, $n = 16$ and 10) in the presence of hydrogen-terminated silicon (H–Si(111) and H–Si(100)). In spite of the great theoretical and practical interest in both self-assembled monolayers[1,2] and silicon, there have been, to our knowledge, no reports of a covalent linkage of densely packed, long alkyl chains directly to a silicon surface.[3,4] We hypothesized that alkyl monolayers could be created by the following reactions of a radical, R$^\cdot$, at a silicon surface:

$$\text{Si–H} + \text{R}^\bullet \rightarrow \text{Si}^\bullet + \text{RH}$$

$$\text{Si}^\bullet + \text{R}^\bullet \rightarrow \text{Si–R}$$

We also note the possibility that the silicon dangling bond may induce decomposition of some diacyl peroxide to create surface-bound species.[5] In this paper we employ the thermal decomposition of diacyl peroxides to produce alkyl radicals, $CH_3(CH_2)_n^\cdot$, via $CH_3(CH_2)_nCOO^\cdot$. Infrared absorption, X-ray photoelectron spectroscopy (XPS), surface wetting, and ellipsometric measurements reveal that the alkyl groups are packed as densely in these new self-assembled monolayers as in those formed from alkyltrichlorosilanes on oxidized silicon or from alkanethiols on gold and indicate a high coverage of carbon bound directly to silicon.

Superficially oxidized silicon single crystals[6,7] were etched with 40% aqueous NH_4F (Si(111)) or 10% aqueous HF (Si(100)) using the procedures of Higashi and Chabal.[8] XPS confirms the absence of oxidized silicon (chemically shifted Si (2p)). Figure 1a shows the p- and s-polarized attenuated total internal reflection (ATR) infrared (IR) spectra[9] of the resultant H–Si(111) surface. The single sharp absorption at 2083.9 cm^{-1} in the p-spectrum and the absence of absorption in the s-spectrum confirm, as expected,[8] that the monohydride is oriented exactly perpendicular to the (111) plane and is the only significant silicon hydride species on the surface. H–Si(100) samples showed peaks due to SiH_n (n = 1, 2, 3) as expected.[8]

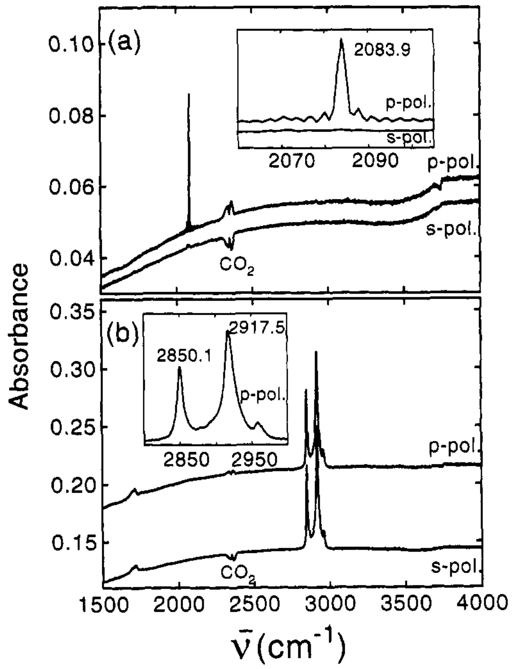

Figure 1. Infrared absorption spectra referenced to a clean, superficially oxidized silicon surface. (a) Bare H–Si(111) surface. (b) Monolayer-coated surface formed from $[CH_3(CH_2)_{16}C(O)O]_2$ and H–Si(111).

H–Si samples were placed in a vial with sufficient solid $[CH_3(CH_2)_nC(O)O]_2$[10,11] to completely cover the sample when molten. ***Caution*: acyl peroxides, particularly those with a high oxygen-to-carbon ratio, can be contact explosives!** The vial was then evacuated with a liquid nitrogen-trapped mechanical pump, heated until the material melted at about 75 °C, back-filled with argon, and heated to 90–100 °C to pyrolyze the peroxide. Gas evolved vigorously for 1 h, after which the sample was removed from the still molten reaction mixture, rinsed with hexane and ethanol, and sonicated for 5–10 min in CH_2Cl_2. The resultant surfaces were hydrophobic, and an ethanol film readily retracted from them.

Figure 1b shows the IR spectra of the $[CH_3(CH_2)_{16}C(O)O]_2$/H–Si(111) monolayer. Both the strong absorbance and the position of the asymmetric methylene stretch (2917.5 cm^{-1}) suggest the formation of a close-packed monolayer. The thickness was measured by ellipsometry to be 25 Å, a value appropriate for such an array of densely packed, nearly perpendicular alkyl chains.[12] The advancing contact angles (θ_a) for water and hexadecane (HD) were measured to be 112° and 46°, respectively, suggesting that the surface is methyl-terminated.[13] XPS shows the presence of C (1s), O (1s), and Si (2p) peaks and no discernible signal for F (1s) or oxidized Si (chemically shifted Si (2p)) signal.

Table I compares some physical properties of the new silicon monolayers with those measured in our lab for similar chain-

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(1) Nuzzo, R. G.; Allara, D. L. *J. Am. Chem. Soc.* **1983,** *105,* 4481–4483.

(2) Maoz, R.; Sagiv, J. J. *J. Colloid Interface Sci.* **1984,** *100,* 465–496.

(3) Other workers have looked at the gas-phase reactivity of silicon with small carbon-containing molecules[4a] 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, respectively.[4b]

(4) (a) Cheng, C. C.; Taylor, P. A.; Wallace, R. M.; Gutleben, H.; Clemen, L.; Colaianni, M. L.; Chen, P. J.; Weinberg, W. H.; Choyke, W. J.; Yates, J. T. *Thin Solid Films* **1993,** *225,* 196–202. Bent, B. E.; Kao, C.-T.; Zegarski, B. R.; Dubois, L. H.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1991,** *113,* 9112–9119. (b) Cullen, G. W.; Amick, J. A; Gerlich, D. *J. Electrochem. Soc.* **1962,** *109,* 124–127. Spool, A. M.; Daube, K. A.; Mallouk, T. E.; Belmont, J. A.; Wrighton, M. S. *J. Am. Chem. Soc.* **1986,** *108,* 3155–3157. Sheen, C. W.; Shi, J.-X.; Martensson, J.; Parikh, A. N.; Allara, D. L. *J. Am. Chem. Soc.* **1992,** *114,* 1514–1515.

(5) Kochi, J. K. *Free Radicals*; John Wiley: New York, 1973; pp 116–120.

(6) Si ATR plates and wafers were etched with aqueous fluoride solutions and superficially oxidized by exposure to a 3:1 mixture of concentrated H_2SO_4 and 30% H_2O_2 at ~100 °C for 2 h, followed by a 1:1 mixture of concentrated NH_4OH and 30% H_2O_2 for 15 min,[7] and finally by the acid peroxide solution at room temperature. Rinses with water (MilliQ) were performed after each step. ***Caution*: basic and acidic solutions of H_2O_2 are exceedingly dangerous and should be handled with great care.**

(7) Kern, W.; Puotinen, D. A. *RCA Rev.* **1970,** *31,* 187–206.

(8) Higashi, G. S.; Chabal, G. W.; Trucks, G. W.; Raghavachari, K. *Appl. Phys. Lett.* **1990,** *56,* 656–658.

(9) All absorption spectra were taken with 45°, trapezoidal, 50- × 20- × 1-mm Si(100) and Si(111) ATR plates from Harrick Scientific.

(10) The compounds were prepared using a modified procedure of Fieser and Oxford.[11] $[CH_3(CH_2)_{16}C(O)O]_2$: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.42 (s), 1.71 (m), 1.25 (m), 0.89 (t); IR (melt, cm^{-1}) 2914.9 (s), 2850.3 (s), 1806.1 (m), 1776.2 (s). Anal. Calcd for $C_{36}H_{70}O_4$: C, 76.27; H, 12.44. Found: C, 76.17; H, 12.55. $[CH_3(CH_2)_{10}C(O)O]_2$: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.42 (s), 1.71 (m), 1.25 (m), 0.89 (t). Anal. Calcd for $C_{24}H_{46}O_4$: C, 72.31; H, 11.63. Found: C, 72.38; H, 11.81.

(11) Fieser, L. F.; Oxford, A. E. *J. Am. Chem. Soc.* **1942,** *64,* 2060–2065.

(12) Because the silicon under an organic film might oxidize with time and give deceptively high thicknesses, infrared absorption generally gives more reasonable estimates of mass coverage on silicon substrates. However, in this case, the measured absence of oxidized silicon by XPS validates the ellipsometry. Ellisometry is actually more reliable for films on inert metals than infrared absorption because molecular orientation dramatically changes their measured absorption intensities.

(13) Fox, H. W.; Zisman, W. A. *J. Colloid Sci.* **1952,** *7,* 428.

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Table I. Physical Properties of Monolayers on Silicon, Oxidized Silicon, and Gold

	asymmetric methylene stretch[a]		contact angles[b]		
system	position (cm^{-1})	area (arb)	$\theta_{a/r}$ (H_2O)	$\theta_{a/r}$ (HD)	thickness[c] (Å)
$[CH_3(CH_2)_{16}COO]_2$/H–Si(111)	2917.5	1.81	112°/104°	46°/43.5°	25
$CH_3(CH_2)_{17}SH$/Au	2917.9		114°/98.5°	50°/40.5°	28
$CH_3(CH_2)_{17}SiCl_3$/oxidized Si	2917.3	1.81	112°/109°	46.5°/45°	25
$[CH_3(CH_2)_{10}COO]_2$/H–Si(111)	2921.0	1.05	112°/103.5°	40.5°/36°	17
$[CH_3(CH_2)_{10}COO]_2$/H–Si(100)	2922.9	1.08	112.5°/104°	33°/30°	16 ± 2
$CH_3(CH_2)_{11}SH$/Au	2919.2		113.5°/103.5°	47°/38.5°	17
$CH_3(CH_2)_{11}SiCl_3$/oxidized Si	2921.7	1.09	114°/112°	42°/39°	17
$CH_3(CH_2)_{16}COOH$/H–Si(111)	2923.3	0.21			
$CH_3(CH_2)_{16}COCl$/H–Si(111)	2925.8	0.47			

[a] Area calculated as (peak height) × (full width at half-height). Uncertainties in measurements: position, 0.3 cm^{-1}; height, ±3%; area, ±10%. [b] Advancing/receding contact angles for water and hexadecane (HD); uncertainty, ±1°. [c] Ellipsometric thicknesses ($n_f = 1.46$); uncertainty, ±1 Å.

length trichlorosilanes on oxidized silicon[2] and for thiols on gold (on a Cr adhesion layer on silicon).[1] By IR, ellipsometry, and wetting, the properties of the three monolayers containing 17 and 18 carbons are nearly identical and indicate that all are closely-packed, methyl-terminated surfaces. From experiments with shorter-chain species, we observe that the $[CH_3(CH_2)_{10}C(O)O]_2$/H–Si(111) and $CH_3(CH_2)_{11}SiCl_3$/oxidized Si surfaces have similar properties though both appear somewhat less ordered than $CH_3(CH_2)_{11}SH$/Au. In addition, IR and θ_a(HD) reveal that $[CH_3(CH_2)_{10}C(O)O]_2$/H–Si(100) films are not as closely packed as those on Si(111). We attribute the variance in monolayer packing on Si(100) and Si(111) to their different initial hydrogen terminations and different silicon surface structures. Moreover, the attempted reactions of H–Si(111) with stearic acid and with octanoyl chloride gave surfaces with submonolayer coverages (10–25%) of disordered and presumably physisorbed material.

Stability tests of the films formed from the longer-chain acyl peroxide and from the longer trichlorosilane show the two systems to be comparably robust. After 2 h in boiling chloroform and 1 h in boiling water, the peak positions and areas of the asymmetric CH_2 stretch had shifted in the following way: $[CH_3(CH_2)_{16}C(O)O]_2$/H–Si(111), (2917.5 cm^{-1}, 1.8 cm^{-1}) to (2919.9 cm^{-1}, 1.2 cm^{-1}); $CH_3(CH_2)_{17}SiCl_3$/oxidized Si, (2917.3 cm^{-1}, 1.8 cm^{-1}) to (2919.9 cm^{-1}, 1.5 cm^{-1}). On the other hand, only 30 min in boiling $CHCl_3$ were required for a similar effect on $CH_3(CH_2)_{17}SH$/Au: 2917.9 cm^{-1} to 2920.9 cm^{-1}, where the thickness decreased by 30%.[12]

We note that the two obvious covalent linkages to the surface are a Si–CH_2- bond or a Si–OC(O)CH_2- bond and that the nearest-neighbor distance between silicon atoms on the (111) surface (3.84 Å) is too small to allow complete replacement of surface hydrogens by alkyl chains (diameter, 4.6 Å[14]). We also observe that the Si–H stretch disappears entirely upon formation of the monolayer but that the O–H stretch, which had disappeared in the hydrogen-terminated surface (note the broad peak at 3400 cm^{-1}) largely returns after formation of the monolayer. XPS confirms the additional oxygen. The presence of a weak carbonyl at 1715 cm^{-1} suggests the formation of some Si–OC(O)CH_2-linked chains. From an analysis of IR-ATR spectra of long-chain Langmuir–Blodgett films of fatty acids on oxidized silicon,[15] we conclude that this corresponds to approximately 30% of a monolayer. A Si–OC(O)CH_2-linked chain is expected to be readily hydrolyzed.[16] And, indeed, the stability experiments described above confirm that approximately 30% of the monolayer is removed under harsh hydrolytic conditions. We conclude that the majority linkage is Si–CH_2- and that sites that do not bind to alkyl chains react with oxygen from the acyl peroxide or adventitious water to form surface silanols.

We have prepared a new class of robust, covalently-bound alkyl monolayers on silicon where the majority linkage is a direct bond of C to Si. In subsequent work we will explore the structure and formation of the monolayers, related monolayer formation chemistry, and the formation of functionalized monolayers.

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(14) Chidsey, C. E. D.; Loiacono, D. N. *Langmuir* **1990**, *6*, 682–691.

(15) Davies, G. H.; Yarwood, J. *Spectrochim. Acta* **1987**, *43A*, 1619–1923.

(16) The acyloxy group should be a better leaving group than the alkoxy, which is in turn much better than the alkyl group. Early and preliminary experiments with the dialkyl peroxide $[CH_3(CH_2)_{11}O]_2$ on Si(100) yielded close-packed monolayers (presumably through a Si–O linkage) that were completely removed by Soxhlet extraction in CH_2Cl_2 where no provision was made to exclude adventitious water.