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Infrared Vibrational Spectroscopy of Isotopically Labeled Ethyl-Terminated Si(111) Surfaces Prepared Using a Two-Step Chlorination/Alkylation Procedure

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Fourier transform infrared (FTIR) spectroscopy was used to investigate C_2H_5–Si(111) surfaces prepared using a chlorination/alkylation method. After alkylation, in addition to ethyl groups, such surfaces showed the presence of hydrogen bonded to atop silicon surface atoms. Systematic isotopic substitution of protic solvents and reagents with their fully or partially deuterated counterparts revealed the origin of the surface-bound hydrogen on the C_2H_5–Si(111) surfaces. The presence or absence of the Si–H stretch at 2080 cm^{-1} and the Si–D stretch at ~1510 cm^{-1}, respectively, indicated that the hydrogen originated from the methyl group of the ethyl Grignard reagent.

I. Introduction

Functionalization of silicon surfaces by chemically bonding small molecules to exposed silicon sites provides a passivation method that avoids high temperatures and can be applied to nanostructured surfaces.[1–7] Alkylation using a two-step chlorination/alkylation process has been shown to produce silicon surfaces that are passivated chemically and electrically.[8–12] Specifically, alkylated silicon surfaces are less susceptible to oxidation in air than are hydrogen-terminated silicon surfaces, and the recombination velocities of CH_3–Si(111) surfaces are very low, typically having values of $10-100$ cm s^{-1}. Scanning tunneling microscopy (STM), infrared (IR), and soft X-ray photoemission spectroscopy (SXPS) data have indicated that, consistent with steric considerations, alkylation with methyl groups terminates an unreconstructed silicon surface with Si–C bonds on nearly all of the silicon atop sites.[8,11,13–18]

Alkylation with ethyl groups, however, cannot produce 100% termination of Si(111) 1×1 atop sites with Si–C bonds because of unfavorable steric interactions between methylene hydrogens on adjacent ethyl moieties.[14,18] XPS studies have indicated that alkylation of a Si–Cl surface yields ethyl groups on 60–90% of the Si atop sites.[14,18] The termination of the remaining, nonethyl-terminated, silicon sites is of interest to better define the ethylated Si(111) surface.[16] For methyl- and ethyl-functionalized Si(111) surfaces, no silicon oxide has been detected by SXPS, and only silicon, oxygen, and carbon have been detected on the surface.[15] For CH_3–Si(111) surfaces, no IR signatures are present other than those ascribable to the CH_3–Si(111) unit and to adventitious carbon, except for signals arising from relatively small amounts (less than 10% of a monolayer) of silicon oxides.[15] For ethyl-terminated silicon surfaces, no silicon oxides are detectable by transmission IR spectroscopy, but ~15% of a monolayer of silicon atop sites are terminated with Si–H bonds.[16] The presence of Si–H termination is consistent with the hypothesis that termination with ethyl groups cannot produce Si–C bonding to every Si atop site on the unrecon-

structed Si(111) surface. The presence of Si–H bonding as well as the predominance of Si–C bonding is consistent with the observed low surface recombination velocities of C_2H_5–Si(111) surfaces and with the relatively high (60–90%) coverages of ethyl groups that are obtained when the ethylation process is performed from the high-energy, metastable, Si–Cl surface produced using the two-step chlorination/alkylation procedure.[14,18]

In this work, we have performed isotopic labeling studies on C_2H_5–Si(111) surfaces to buttress the assignment of the non-Si–C-terminated surface sites as being terminated by Si–H bonds and to ascertain the origin of the hydrogen in the Si–H surface species. FTIR data have been obtained for the alkylation of Cl–Si(111) surfaces with $-1,1\text{-}d_2\text{-}CD_2CH_3$ or $-2,2,2\text{-}d_3\text{-}CH_2CD_3$ in protic tetrahydrofuran (THF), with $-C_2H_5$ or $-C_2D_5$ in THF and deuterated THF (THF-d_8) as well as when the sample was exposed to and rinsed with protic or deuterated solvents. These isotopic labeling studies have also enabled investigation of the C–H IR stretching regions of methyl- and ethyl-terminated Si(111) surfaces.

II. Experimental Section

A. Materials and Methods. All chemicals were used as received. Water was obtained from a Barnstead Nanopure system and had a resistivity of ≥18.3 MΩ cm. The float-zone grown Si(111) wafers (Silicon Quest International, Santa Clara, CA) were polished on both sides and were n-type, with a resistivity of 63–77 ohm cm.

1. Synthesis of 1 M Ethyl Grignard Reagents. To prepare C_2D_5MgBr in THF, magnesium turnings (0.711 g, 29.2 mmol) were polished, using a mortar and pestle, in a $N_2(g)$-purged glovebox. The magnesium turnings were then added to a round-bottomed flask that contained 26 mL of THF (Sigma Aldrich, anhydrous, inhibitor free) and a magnetic stir bar. While maintaining the THF in an ice bath under constant stirring, ethyl-d_5 bromide (3.00 g, 26.3 mmol) was added dropwise through an addition funnel. With constant stirring, the solution was then allowed to come to room temperature for 30 min, transferred to a Schlenk flask by use of a cannula, and placed in a $N_2(g)$-purged glovebox until further use. Analogous procedures were used to synthesize $2,2,2\text{-}d_3\text{-}D_3CH_2CMgBr$ in THF, $1,1\text{-}d_2\text{-}$

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H_3CD_2CMgBr in THF, H_3CH_2CMgBr in THF-d_8, and D_3CD_2-$CMgBr$ in THF-d_8.

2. Oxidation of and Removal of Organic Contaminants from the Si(111) Surface. Si wafers were cut into (1.5 × 1.5 cm) squares for grazing angle total internal reflection (GATR) measurements. The Si wafers were then rinsed with water, methanol, acetone, methanol, and finally water. The wafers were cleaned using the RCA 1 clean ($H_2O:NH_4OH$ (28−30 wt %): H_2O_2 (29−32 wt %), 5:1:1 by volume at 70 °C for 15 min) and RCA 2 clean ($H_2O:HCl$ (36.5−38 wt %):H_2O_2, 5:1:1 by volume at 70 °C for 10 min) solutions. During the cleaning procedure, we agitated the wafers occasionally, and care was taken to keep the temperature constant within ± 2 °C. Directly following the RCA 2 clean, the samples were washed with water, dried under a stream of $N_2(g)$, and stored until further use.

3. Hydrogen Termination of Si(111) Samples. Before immersion for 45 s in 6 M HF(aq) [prepared by dilution of 49% HF(aq) (semiconductor grade, Transene Company, Inc., Danvers, MA)], the silicon wafers were rinsed sequentially with water, methanol, acetone, methanol, and water. The Si(111) samples were then removed from the HF(aq), rinsed with H_2O, and immediately immersed into an 11 M NH_4F(aq) (semiconductor grade, Transene Company, Inc.) solution that had been purged with ultrahigh purity Ar for at least 45 min. The NH_4F(aq) was continuously purged during the etching process, and agitation of the sample prevented the accumulation of bubbles on the wafer. After 10 min of etching, the samples were removed from the solution, rinsed with H_2O, and immediately transferred into a $N_2(g)$-purged flush box that contained less than 10 ppm of $O_2(g)$.

4. Chlorination of H−Si(111). Hydrogen-terminated Si(111) samples were immersed in a saturated solution of PCl_5 (99.998% metal basis, Alfa Aesar) in chlorobenzene (Anhydrous, 99.8%, Sigma Aldrich) to which a small amount of benzoyl peroxide (Aldrich reagent grade, 97%, Sigma Aldrich) had been added. The solutions were heated to 90−95 °C for 45 min, after which the wafers were removed from the solution and liberally rinsed with THF. This procedure has been shown to result in fully Cl-terminated Si(111) surfaces, with little surface roughening.[19] Samples were then transferred immediately to the alkylating solution.

5. Alkylation of Cl−Si(111) Samples. Immediately after chlorination, the Cl-terminated Si(111) wafers were immersed in either a 1 M solution of CH_3MgCl in THF, a 1 M solution of C_2H_5MgBr in THF or THF-d_8, a 1 M solution of C_2D_5MgBr in THF or THF-d_8, a 1 M solution of 2,2,2-d_3-D_3CH_2CMgBr in THF, or a 1 M solution of 1,1-d_2-H_3CD_2CMgBr in THF, and were then heated to 70−75 °C. The methyl Grignard reagent was heated for 3 h, while ethyl Grignard reagents were heated for 5 h.

6. Postalkylation Workup of Si(111) Surfaces. After the reaction, the alkylated samples were removed from the reaction vessel and rinsed with copious amounts of THF, followed by a rinse with methanol. Occasionally the THF rinse step was omitted and was found to have no measurable effect on the surface quality as indicated by a lack of change in the intensity or position of the characteristic CH_3−, C_2H_5−, SiO_x, or Si−H FTIR modes. The samples were then immersed in methanol and removed from the glovebox, after which they were sonicated for 5 min followed by sonication in acetonitrile for an additional 5 min. Occasional rinsing with water was needed to remove particles from the surface of the sample. To synthesize ethyl- or ethyl-d_5- terminated surfaces using fully deuterated solvents,
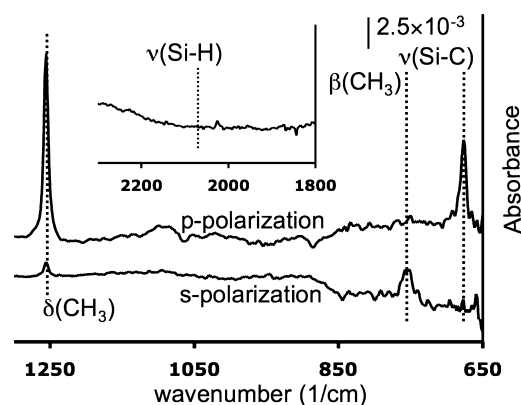

Figure 1. FTIR spectra of a methyl-terminated Si(111) surface. Top and bottom spectra were obtained using p-polarized and s-polarized light, respectively. Spectra were referenced to a C_2D_5−Si(111) surface, while the insert was referenced to the blank GATR crystal.

methanol-d_4, THF-d_8, acetonitrile-d_3, and water-d_2 were used in the postalkylation workup steps.

B. Instrumentation. FTIR spectra were collected using a Thermo Scientific Nicolet 6700 optical spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector and a purified air purge. The spectra were recorded using a GATR accessory (Harrick Scientific Products, Inc.) in which samples were first cleaned with methyl ethyl ketone and then pressed against a hemispherical Ge crystal and illuminated at a fixed, 65°, incident angle. Intimate contact between the sample and the Ge crystal was produced by use of a slip clutch that applied 56 oz. in. (0.39 N m) of torque to the fastening screw. Using this procedure, peak areas were reproducible to within 30% for different samples that were prepared and handled using nominally identical procedures and were reproducible to within 10% for the same sample that was sequentially inserted into, removed from, and then reinserted into the GATR instrumentation. After mounting the sample in the spectrometer, the sample compartment was purged with purified air for at least 1 h before collection of spectra. All spectra were the averages of 6000 consecutive scans that were recorded at a resolution of 4 cm^{-1}, with the aperture maximized for this particular spectral resolution. Polarized spectra were obtained using a computer-controlled polarizer that was mounted inside the spectrometer. The throughput, with the GATR accessory and polarizer installed, was 4%.

III. Results

A. Methyl-Terminated Si(111) Surfaces. Figures 1 and 2 show the attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra of a CH_3−Si(111) surface prepared using 1 M CH_3MgCl in THF. Within the limits of detection, no Si−H stretch was detectable in the 2080 cm^{-1} region (Figure 1, insert). Peaks were observed at 1256, 1100, 754, and 678 cm^{-1} (Figure 1), and at 2960, 2930, 2909, and 2858 cm^{-1} (Figure 2). The peaks at 2909, 1256, 1100, and 678 cm^{-1} were primarily observed in the spectrum obtained using p-polarized light, whereas the peaks at 754, 2858, 2930, and 2960 cm^{-1} were primarily observed using s-polarized light. The ATR-FTIR results are summarized in Table 1.

B. Ethyl-Terminated Si(111) Surfaces. Figure 3 shows the ATR-FTIR spectra of a C_2H_5-terminated Si(111) surface. The surface was functionalized using all protic solvents and reagents. The peak centered around 2080 cm^{-1} was only observed using p-polarized light. Furthermore, two main peaks at 2930 and 2880

Ethyl-Terminated Si(111) Surfaces

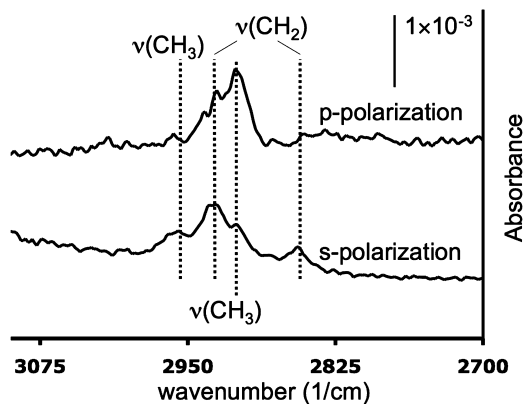*J. Phys. Chem. C, Vol. 113, No. 34, 2009* **15241**

Figure 2. FTIR spectra of the C−H stretching region of a methyl-terminated Si(111) surface. Top and bottom spectra were obtained using p-polarized and s-polarized light, respectively. A C_2D_5−Si(111) surface was used as a reference.

TABLE 1: Assignment of IR Peaks Observed on Functionalized Si(111) Surfaces

−R	ν (cm^{-1})	IR peak location assignment	polarization
−CH$_3$	2960	ν_a(C−H)$_{CH3}$[16]	s, p(weak)
	2930	ν_a(C−H)$_{CH2}$ (adventitious)[16]	s
	2909	ν_s(C−H)$_{CH3}$[16]	p
	2858	ν_s(C−H)$_{CH2}$ (adventitious)[16]	s
	1256	δ_s(C−H)$_{CH3}$[16]	p
	1100	TO (Si−O−Si)[16]	s, p
	754	ρ(C−H)$_{CH3}$[16]	s
	678	ν(Si−C)$_{CH3}$[21]	p
−C$_2$H$_5$	2960	ν_a(C−H)$_{CH3}$[22]	s
	2930	ν_s(C−H)$_{CH3}$[23,24]	s(weak), p
	2905	ν_a(C−H)$_{CH2}$	s, p
	2880	ν_s(C−H)$_{CH3}$[23,24]	s(weak), p
	2850	ν_a(C−H)$_{CH2}$[23,24]	s
	2080	ν(Si−H)[32]	p
	1464	deformation$_a$(CH$_3$)[24]	p
	1378	deformation$_s$(CH$_3$)[24]	p
−C$_2$D$_5$	2214		p
	2179	$\nu_{a,s}$(C−D)$_{CH3}$	p
	2135	$\nu_{a,s}$(C−D)$_{CH2}$[27]	p
	2087		p
	1510	ν(Si−D)[25,26]	p
−C$_2$H$_2$D$_3$	2205		s(weak), p
	2129	$\nu_{a,s}$(C−D)$_{CH3}$[27]	s(weak), p
	2084		s(weak), p
	1510	ν(Si−D)[25,26]	p
−C$_2$H$_3$D$_2$	2080	ν(Si−H))[32]	p
	1464	deformation$_a$(CH$_3$)[24]	p
	1378	deformation$_s$(CH$_3$)[24]	p

cm^{-1} were observed in the C−H stretching region using p-polarized light, whereas when s-polarized light was used additional peaks at 2960 and 2905 cm^{-1} and a shoulder at 2850 cm^{-1} were observed. Two peaks at 1464 cm^{-1} and 1378 cm^{-1} were also observed using p-polarized but not s-polarized light.

The ATR-FTIR spectrum of a C_2H_5-terminated Si(111) surface synthesized using C_2H_5MgBr in THF-d$_8$ with an all protic workup showed a peak centered around 2080 cm^{-1}, indicating that the Si−H bond was still present (Figure 4, insert). The ATR-FTIR spectrum of a C_2H_5-terminated Si(111) surface synthesized using C_2H_5MgBr in THF-d$_8$ and only deuterated solvents in the workup steps, with the THF rinse omitted, also showed a broad peak centered around 2080 cm^{-1} in the p-polarized spectrum (Figure 4).

C. Ethyl-d$_5$-Terminated Si(111) Surfaces. Figure 5 shows the ATR-FTIR spectrum of a C_2D_5-terminated Si(111) surface that had been synthesized using C_2D_5MgBr in THF, followed
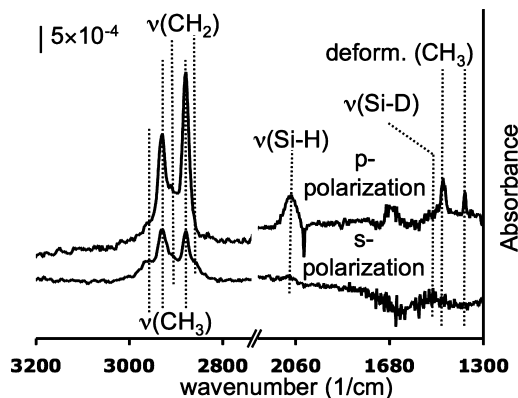

Figure 3. Polarized FTIR spectra for an ethylated Si(111) surface prepared using all protic solvents. Top and bottom spectra are p- and s-polarized, respectively. A broad peak was present, centered around 2080 cm^{-1}, only in the p-polarized spectrum. Note the absence of a peak at ∼1510 cm^{-1}. The 1300−2100 cm^{-1} region was referenced to a CH$_3$−Si(111) surface, and the 2700−3200 cm^{-1} region was referenced to a C_2D_5−Si(111) surface.
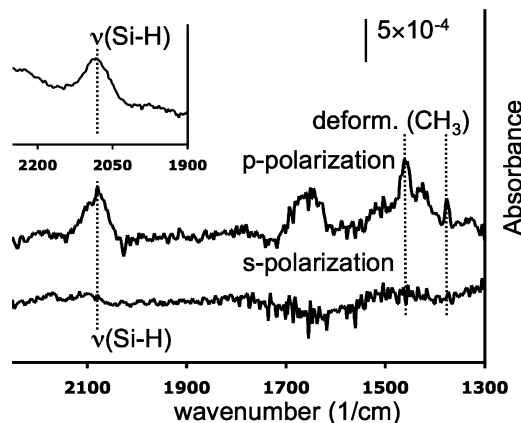

Figure 4. FTIR spectrum obtained for an ethyl-terminated Si(111) surface synthesized using C_2H_5MgBr in THF-d$_8$ followed by an all deuterated workup. Top and bottom spectra are p- and s-polarized, respectively. A broad peak centered around 2080 cm^{-1} was observed. The p-polarized FTIR spectrum of an ethyl-terminated Si(111) surface synthesized using C_2H_5MgBr in THF-d$_8$, followed by an all protic workup showed a broad peak centered around 2080 cm^{-1} (insert). Spectra were referenced to a CH$_3$−Si(111) surface.

by an all protic workup. Several peaks were observed in the 2100 cm^{-1} region as well as a peak centered at ∼1510 cm^{-1}. To reveal the possible presence of a Si−H stretch convoluted with the C−D stretching signals, a C_2D_5-terminated Si(111) surface was prepared using only deuterated solvents. Figure 6 compares the 2100 cm^{-1} region of two ethyl-d$_5$-derivatized Si(111) surfaces in which one surface was prepared using all protonated solvents and the other using all deuterated solvents. Both spectra were obtained using p-polarized light.

D. Ethyl-d$_3$-Terminated Si(111) Surfaces. Figure 7 shows the ATR-FTIR spectrum of a 2,2,2-d$_3$-D$_3$CH$_2$C-terminated Si(111) surface that had been synthesized using 2,2,2-d$_3$-D$_3$CH$_2$CMgBr in THF, followed by an all protic workup. Three peaks were observed in the 2100 cm^{-1} region, at 2205, 2129, and 2084 cm^{-1} as well as a peak centered at ∼1510 cm^{-1}. The peaks at 2205, 2129, and 2084 cm^{-1} were present in the spectrum obtained using p-polarized light, but their intensity was greatly reduced when s-polarized light was used. The peak at ∼1510 cm^{-1} was only present in the spectrum obtained using p-polarized light.

E. Ethyl-d$_2$-Terminated Si(111) Surfaces. Figure 8 shows the ATR-FTIR spectrum of a 1,1-d$_2$-H$_3$CD$_2$C-terminated Si(111)

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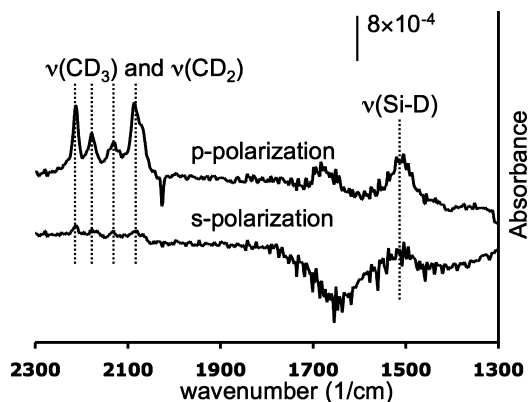
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Figure 5. FTIR spectrum of an ethyl-d_5-terminated Si(111) surface, showing four peaks centered around 2150 cm^{-1} as well as a broad peak centered around 1510 cm^{-1}. Spectra were referenced to a CH$_3$−Si(111) surface.
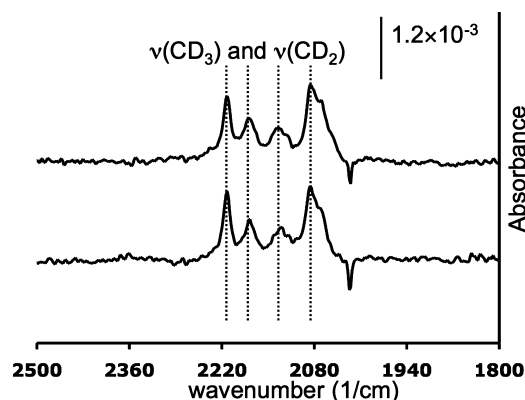

Figure 6. Top spectrum is of an ethyl-d_5-derivatized Si(111) surface prepared using all deuterated solvents. Bottom spectrum is of an ethyl-d_5-derivatized Si(111) surface prepared using all protic solvents. Both spectra were obtained using p-polarized light. Spectra were referenced to a CH$_3$−Si(111) surface.
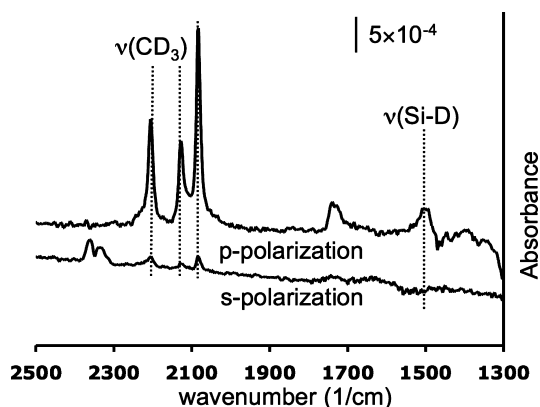

Figure 7. FTIR spectrum of an ethyl-d_3-terminated Si(111) surface, showing three peaks centered around 2150 cm^{-1} as well as a broad peak centered around 1510 cm^{-1}. Spectra were referenced to a CH$_3$−Si(111) surface.

surface that had been synthesized using 1,1-d_2-H$_3$CD$_2$CMgBr in THF, followed by an all protic workup. A peak centered around 2080 cm^{-1} was observed, as well as peaks at 1464 and 1378 cm^{-1}. These peaks were only observed using p-polarized light.

IV. Discussion

Previous transmission FTIR studies have shown that the Si−H on ethyl-terminated Si surfaces prepared by the two-step
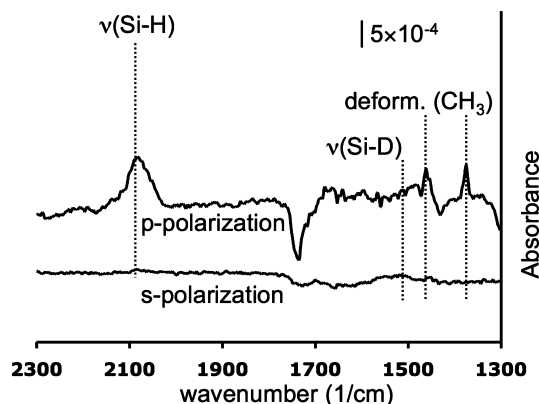

Figure 8. FTIR spectrum of an ethyl-d_2-terminated Si(111) surface, showing a peak centered around 2080 cm^{-1}, two peaks at 1464 and 1378 cm^{-1}, and the absence of a peak centered around 1510 cm^{-1}. Spectra were referenced to a CH$_3$−Si(111) surface.

chlorination/alkylation procedure appears only after alkylation of the fully Cl-terminated Si(111) surface.[16,19] The chlorine is thus replaced by hydrogen during the alkylation. The present work has used deuterium substitution of the reactants and solvents in the alkylation reaction to determine the source of the hydrogen atom in the observed surface Si−H functionality.

The Si−H and oxidized Si surfaces were not suitable as FTIR references because the cleaning step (wiping with methyl ethyl ketone) prior to sample mounting on the GATR lead to partial oxidation of the Si−H surface (as shown by transmission FTIR and GATR-FTIR) and H-SiO$_x$ formation, with spectral features that overlapped with the Si−H as well as the SiO$_x$ region. Similarly, H-SiO$_x$ species were shown (using the GATR) to be present on oxidized Si surfaces, making this surface also unsuitable as a reference.

The oxide region of the alkylated Si(111) surfaces has been investigated previously, using SXPS[15] and FTIR.[16] The deuterated and partially deuterated surfaces were assumed to be similar in composition to the ethylated surface with respect to the amount and form of surficial silicon oxide.

GATR spectroscopy is more sensitive by a factor of ∼30 to p-polarized rather than s-polarized light. However, in the GATR configuration, s-polarized modes are nevertheless enhanced in absolute intensity as compared to those of transmission FTIR spectroscopy.[20] For p-polarized light, the absolute intensity of the p-polarized methyl umbrella mode increased by a factor of ∼40 in GATR relative to that of transmission IR, whereas for s-polarized light the absolute intensity of the s-polarized 754 cm^{-1} peak increased by a factor of ∼1.5 relative to that of the transmission IR.[16] This ratio of ∼27 relative enhancement of p- versus s-polarized modes in GATR versus transmission IR is thus in reasonable agreement with theoretical predictions.[20]

A. Methyl-Terminated Si(111) Surfaces. The spectrum of the methyl-terminated Si(111) surface (Figures 1 and 2) is consistent with that reported previously.[16] Within the limits of detection, no Si−H stretch was observed in the 2080 cm^{-1} region (Figure 1, insert). Peaks at 1256, 1100, 754, 678, 2909, and 2960 cm^{-1} have previously been assigned as corresponding to the CH$_3$ umbrella mode, Si−O−Si transverse optical mode,[21] Si−CH$_3$ rocking mode, Si−C stretch, CH$_3$ symmetric stretch, and CH$_3$ asymmetric stretch, respectively. Additional peaks in the C−H stretching region (2930 and 2858 cm^{-1}) are attributable to adventitious carbon (Table 1), which if present in the optical train would absorb s- and p-polarized light equally and would also account for the observation of rather strong absorption peaks in the GATR arrangement when s-polarized light was used. The

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methyl ethyl ketone cleaning step as well as trace amounts of hydrocarbons in the purified air purge are both expected to contribute to the presence of adventitious carbon in the GATR apparatus.

The peaks at 2909, 1256, and 678 cm^{-1} were prominent features only in p-polarized spectra. In contrast, the 754 and 2960 cm^{-1} peaks were prominent only in s-polarized spectra. The polarization of these peaks supports the assignments that the CH$_3$ symmetric stretch, CH$_3$ umbrella mode, and Si—C stretch are all vibrations for which the transition dipole is oriented perpendicular to the plane of the surface, whereas the transition dipoles of the CH$_3$ asymmetric stretch and Si-CH$_3$ rocking mode are oriented parallel or nearly parallel to the silicon surface. Some of the decrease in signal strength for the CH$_3$ symmetric stretch, CH$_3$ umbrella mode, and Si—C stretch could be due to the decrease in sensitivity when going from p- to s-polarized light. However, the presence of an s-polarized absorption band due to the Si—CH$_3$ rocking mode strongly supports previous findings that the CH$_3$ groups are oriented perpendicular to the substrate.[16] Finally, the CH$_3$ umbrella mode at 1256 cm^{-1} was weakly present in s-polarized spectra, which was to be expected because some CH$_3$ groups are likely to have been attached at defect sites and step edges during the chlorination/alkylation procedure, orienting them parallel to the surface.

B. Ethyl-Terminated Si(111) Surfaces. Figure 3 shows the p- and s-polarized spectra, respectively, of the Si—H stretching region. For ethyl-terminated Si(111) surfaces, a broad peak centered around 2080 cm^{-1} was present in the p-polarized spectrum but not in the s-polarized spectrum. This behavior is consistent with previous data in which a peak in the same region has been assigned to hydrogen covalently bonded to the Si(111) surface.[16] The decrease in sensitivity when going from p- to s-polarized light is consistent with this stretch being oriented normal to the surface, although a quantitative interpretation of the observed polarization peak ratio is confounded by the polarization dependence expected for the GATR apparatus. The Si—H stretch has been shown to appear only after the chlorination step, which fully chlorinates the surface,[19] and therefore was not a remnant of the original Si—H surface.[16]

Figure 3 also shows the C—H stretching region for an ethyl-terminated Si(111) surface. As has been observed previously, the p-polarized spectrum showed two strong peaks, at 2930 and 2880 cm^{-1} (Table 1). Using s-polarized light, in addition to the two peaks observed in the p-polarized spectrum that were present at reduced intensities in the s-polarized spectrum, we observed two shoulders at 2960 and 2905 cm^{-1} and a weak shoulder at 2850 cm^{-1}. These peaks can be assigned on the basis of previous work[16] as well as from the experimental and theoretical data for ethyl silane[22] and from IR studies of alkanes.[23,24] The peaks in the p-polarized spectrum at 2930 and 2880 cm^{-1} can be assigned to the CH$_3$ symmetric stretch, with the splitting derived from Fermi resonance interactions with the lower frequency, asymmetric, and CH$_3$ deformation mode.[23,24] The peaks at 2960 and 2905 cm^{-1}, observed using s-polarized light, can be assigned to the CH$_3$ asymmetric stretch and the CH$_2$ asymmetric stretch, respectively. The shoulder at 2850 cm^{-1} is attributed to the CH$_2$ symmetric stretch. The assignment of these peaks is further supported by the use of partially deuterated ethyl Grignard reagents (Figure S1 of the Supporting Information). The ratio of the intensities, when comparing p-polarized spectra to s-polarized spectra, was much greater for the C—D stretching region (Figure 5) than for the C—H stretching region (Figure 3). This is expected because the absorption features in

the C—H stretching region will most likely contain contributions from surface-bound species and from adventitious carbon as described above for the CH$_3$—Si(111) surface, whereas deuterated adventitious carbon is not expected to be present and thus contribute materially to the observed C—D stretching signal intensity. The peaks at 1464 and 1378 cm^{-1} are assigned to the CH$_3$ asymmetric and symmetric deformations, respectively.[24] No peak was observed in the 1510 cm^{-1} region in which the Si—D peak is expected to appear.[25,26]

To test whether the Si—H hydrogen originated from the THF solvent of the Grignard reagent, ethylmagnesium bromide in THF-d$_8$ was used to produce ethyl-terminated Si(111) surfaces. The Si—H peak was still observed after using the Grignard reagent in THF-d$_8$, suggesting that the hydrogen did not originate from the THF solvent (Figure 4, insert).

To determine whether the hydrogen was derived from the postalkylation rinses, a chlorinated Si(111) surface was reacted with ethylmagnesium bromide in THF-d$_8$, followed by a workup in which only deuterated solvents were used. The measured FTIR spectrum clearly displayed a p-polarized peak at 2080 cm^{-1} that can be attributed to the Si—H stretch, with no significant Si—D peak observed at 1510 cm^{-1} (Figure 4). This behavior indicates that the residual hydrogen originated from the Grignard reagent.

The sharp, negative feature at 2025 cm^{-1} (Figures 3 and 4) was not consistently observed, but for completeness is displayed in the spectrum depicted. The features observed near 1700 cm^{-1} are ascribable to residual methyl ethyl ketone, whose use in the cleaning procedure resulted in adsorbed and/or gas-phase residuals in the sample chamber that were readily detectable by very sensitive GATR instrumentation.

C. Ethyl-d$_5$, Ethyl-d$_3$, and Ethyl-d$_2$-Terminated Si(111) Surfaces. Figure 5 shows p- and s-polarized spectra of the Si—H stretching region of an ethyl-terminated Si(111) surface prepared using the ethyl-d$_5$ Grignard reagent. The peaks in this region are assigned to the C—D stretching peaks because the peak positions are consistent with the expected isotopic shift.[27] These peaks indicated that an ethyl-d$_5$-Si(111) surface was successfully prepared, but the position of the C—D stretching peaks obscured observation of the presence or absence of a Si—H peak. However, a new, broad peak that was not present when nondeuterated ethylmagnesium bromide was used to alkylate the surface (Figures 3 and 4) appeared at ~1510 cm^{-1}. The 1510 cm^{-1} peak was present in the p-polarized but not the s-polarized spectrum. This observation is consistent with this vibration having a transition dipole oriented perpendicular to the surface, but could be a result of sensitivity differences between p- and s-polarized light in the GATR versus transmission IR methods. Consistently, previous studies have assigned the Si—D stretch for a deuterium-terminated Si(111) surface to a p-polarized peak at 1516 cm^{-1}.[25,26] As shown in Figure 4, no significant peak at ~1510 cm^{-1} was present when the ethyl-terminated surface was prepared using C$_2$H$_5$MgBr in THF-d$_8$ and deuterated rinse solvents.

To determine whether a residual Si—H peak at ~2080 cm^{-1} was under the peaks assigned to the C—D stretching bands, we prepared an ethyl-d$_5$ surface using deuterated solvents. A detailed comparison of the peak shapes in the Si—H region for this surface to those observed for an ethyl-d$_5$-terminated Si(111) surface that was synthesized using all protic solvents should reveal the presence of any residual hydrogen signal. Figure 6 illustrates that the peak shape remained essentially identical regardless of the solvents used during the reaction and the workup steps, demonstrating that the residual hydrogen arose,

SCHEME 1: Possible Reaction Mechanism Resulting in Hydrogen Termination of an Atop Si Site, with Hydrogen Originating from the Grignard Reactant

SCHEME 2: Possible Reaction Mechanism Resulting in Hydrogen Termination of an Atop Si Site, with Hydrogen Originating from the Grignard Reactant
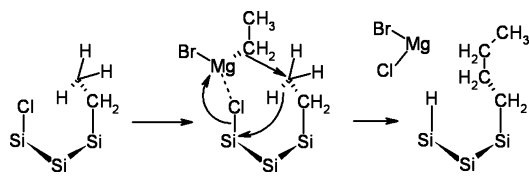

to within the limits of our detection, exclusively from the Grignard reagent. This conclusion is further supported by the fact that the subtraction of the two spectra in Figure 6 showed no residual Si−H peak (Figure S2 of the Supporting Information).

A comparison of the spectra of the ethyl-d$_5$ surface prepared using either all protic or all deuterated solvents also revealed no residual signal in the C−H stretching region. Hence, no side reactions involving the solvents took place to within the limits of detection of the surface-sensitive GATR method (Figure S3 of the Supporting Information).

To determine whether the Si−H hydrogens originated from the α- or β-carbon of the Grignard reagent, we synthesized 2,2,2-d$_3$-ethylmagnesium bromide and 1,1-d$_2$-ethylmagnesium bromide and reacted these species with Cl−Si(111). Figure 7 shows the p- and s-polarized spectra of an ethyl-terminated Si(111) surface synthesized using 2,2,2-d$_3$-ethylmagnesium bromide. Three peaks were observed in the 2100 cm^{-1} region and are assigned as C−D stretching peaks. A broad peak at ∼1510 cm^{-1} was also observed and is assigned to the Si−D stretching mode. The presence of the Si−D stretching mode indicates that the Si−H hydrogen originated from the β-carbon. This conclusion is supported by the p- and s- polarized spectra of the 1,1-d$_2$-ethyl-Si(111) surface, for which a peak at ∼2080 cm^{-1} was present in the p-polarized spectrum but not in the s-polarized spectrum. This peak has been assigned previously to the Si−H stretch. Additionally, no peak at ∼1510 cm^{-1}, attributable to the Si−D stretch, was observed for this surface.

The data presented in Figures 7 and 8 are inconsistent with mechanisms for the functionalization reaction that incorporate the transfer of a hydrogen from the α-carbon of the Grignard reagent to the Si(111) surface. Mechanisms that involve the transfer of the hydrogens on the β-carbon are, however, consistent with the data. A study of the alkylation of silica using Grignard reagents[28] has revealed the presence of Si−H groups formed after the chlorination step, and a mechanism was proposed to explain the reappearance of Si−H groups. An analogous mechanism for transfer of hydrogen from an ethyl group to a silicon atop atom is consistent with the data reported herein (Scheme 1). In this proposed mechanism, the silicon-bound chlorine is activated by coordination to the magnesium of an ethyl Grignard molecule in solution. The chlorine then transfers to the magnesium, forming a magnesium dihalide, while the ethyl group from the Grignard reagent transfers to the terminal carbon of the silicon-bound ethyl group. When a hydrogen from the silicon-bound ethyl group replaces the chlorine on the silicon atop site, two adjacent silicon atop sites, one terminated by hydrogen and the other by a butyl group, are produced. Unfortunately, it is difficult experimentally to distinguish between surface-bound ethyl and butyl groups, especially when the putative butyl moiety would be present in low concentrations on the surface.

Other mechanisms are also possible, including an analogous process in which ionic dissociation of the Si−Cl bond is
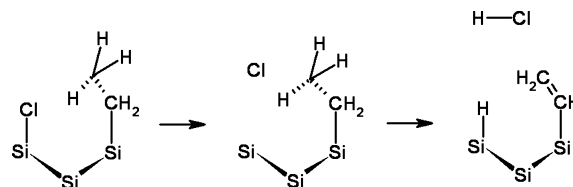
triggered by reduction of the surface by electron transfer from the Grignard reagent, followed by hydrogen abstraction from an adjacent silicon-bound ethyl group (Scheme 2).[14,29] The positively charged ethyl group could then undergo elimination of a hydrogen ion, leading to the formation of a surface-bound vinyl group. This process would result in adjacent atop Si atoms in which one was hydrogen-terminated and the other was vinyl-terminated. The eliminated chlorine and hydrogen would exist in solution as HCl. No C=C−H or C=C−D stretches at 3077 or ∼2250 cm^{-1}, respectively,[30,31] were detectable in the spectra obtained (Figures 3 and 7), but this does not rule out the formation of a surface-bound vinyl species at relatively low concentrations as would be the case in the system investigated.

V. Conclusions

Methyl- and ethyl-terminated Si(111) surfaces have been synthesized using a two-step chlorination/alkylation procedure. In accordance with previous results, the ethyl-terminated Si(111) surface is partially covered by hydrogen covalently linked to silicon atop atoms. The hydrogens do not arise from the original, NH$_4$F(aq)-etched, hydride-terminated surface but rather appear during or after the alkylation step. Systematic isotopic substitution of deuterated reagents and solvents for protic ones was used to deduce the origin of the hydrogen. FTIR spectroscopy, using p- and s-polarized radiation, confirmed the presence of hydrogen covalently bonded to the C$_2$H$_5$−Si(111) surface when protic reagents and solvents were used. Replacement of the protic solvents by deuterated solvents, while leaving the Grignard reagent as the only protic entity, showed that the hydrogen did not significantly arise from any of the solvents used in the reaction. Additionally, comparison of a C$_2$D$_5$−Si(111) surface prepared using either all protic or all deuterated solvents showed that both experiments yielded a surface with a Si−D peak at ∼1510 cm^{-1} but no Si−H peak at 2080 cm^{-1}. Thus, within the limits of detection, the hydrogen on ethylated surfaces arose exclusively from the Grignard reagent. Additionally, the use of partially deuterated Grignard reagents showed that the hydrogen originated from the methyl group and not the methylene group. Finally, when preparing a C$_2$D$_5$−Si(111) surface, a p-polarized signal centered at ∼1510 cm^{-1} was observed. This peak was assigned to the Si−D stretch.

Supporting Information Available: Subtraction results of the C−H stretching region for 1,1-d$_2$-ethyl-Si(111) and 2,2,2-d$_3$-ethyl-Si(111). Subtraction result of the two spectra in Figure 6 and the C−H stretching region of the subtraction result of the spectra from C$_2$D$_5$−Si(111) surfaces synthesized using either

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all protic or all deuterated solvents. This information is available free of charge via the Internet at http://pubs.acs.org.

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JP901792Y