Transmission Infrared Spectroscopy of Methyl- and Ethyl-Terminated Silicon(111) Surfaces

Lauren J. Webb,[†] Sandrine Rivillon,[‡] David J. Michalak,[†] Yves J. Chabal,*[,‡] and Nathan S. Lewis*[,†]

Division of Chemistry and Chemical Engineering, California Institute of Technology, 210 Noyes Laboratory, Pasadena, California 91125, and Department of Chemistry and Chemical Biology, Rutgers University, Piscataway, New Jersey 08502

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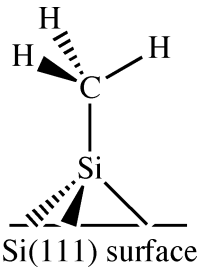
Transmission infrared spectroscopy (TIRS) has been used to investigate the surface-bound species formed in the two-step chlorination/alkylation reaction of crystalline (111)-oriented Si surfaces. Spectra were obtained after hydrogen termination, chlorine termination, and reaction of the Cl−Si(111) surface with CH_3MgX or C_2H_5MgX (X = Cl, Br) to form methyl (CH_3)- or ethyl (C_2H_5)-terminated Si(111) surfaces, respectively. Freshly etched H-terminated Si(111) surfaces that were subsequently chlorinated by immersion in a saturated solution of PCl_5 in chlorobenzene were characterized by complete loss of the Si−H stretching and bending modes at 2083 and 627 cm^{-1}, respectively, and the appearance of Si−Cl modes at 583 and 528 cm^{-1}. TIRS of the CH_3-terminated Si(111) surface exhibited a peak at 1257 cm^{-1} polarized perpendicular to the surface assigned to the C−H symmetrical bending, or "umbrella" motion, of the methyl group. A peak observed at 757 cm^{-1} polarized parallel to the surface was assigned to the C−H rocking motion. Alkyl C−H stretch modes on both the CH_3- and C_2H_5-terminated surfaces were observed near 2900 cm^{-1}. The C_2H_5-terminated Si(111) surface additionally exhibited broad bands at 2068 and 2080 cm^{-1}, respectively, polarized perpendicular to the surface, as well as peaks at 620 and 627 cm^{-1}, respectively, polarized parallel to the surface. These modes were assigned to the Si−H stretching and bending motions, respectively, resulting from H-termination of surface atoms that did not form Si−C bonds during the ethylation reaction.

I. Introduction

Alkylation of silicon(111) surfaces has attracted significant recent attention due to the potential for obtaining molecular level control over the electrical, electrochemical, and chemical properties of Si surfaces.[1−5] Hydrogen-terminated Si(111) surfaces have a very low surface electron−hole recombination velocity,[6] but oxidize rapidly in ambient air, forming a large number of surface electronic trap states.[2] In contrast, alkylated Si surfaces prepared through a two-step chlorination/alkylation procedure show excellent chemical stability and low surface charge carrier recombination rates for extended time periods, even as they are exposed to ambient air.[1,2] Methyl moieties are the only saturated hydrocarbon group which can sterically form a Si−C bond to every atop site on an unreconstructed Si(111) surface, because van der Waals interactions between neighboring methylene units should prevent C_2H_5− and other alkyls from terminating every Si atop site.[7] Furthermore, the sp^3-hybridized Si−C bond on the Si(111) surface should orient the methyl groups on the CH_3-terminated surfaces normal to the surface plane, as shown in Chart 1. This orientation should produce diagnostic signatures and polarizations in the vibrational spectrum of such surfaces. Recent scanning tunneling microscopy[8] and low-energy electron diffraction studies[9] have revealed both short-range and long-range order on CH_3-terminated Si surfaces. However, at present no information is available on the structure of surfaces terminated with alkyls such as C_2H_5− that are sterically precluded from terminating every atop site on an unreconstructed Si(111) surface.

CHART 1



In this report, transmission infrared spectroscopy (TIRS) data are presented for CH_3- and C_2H_5-terminated Si(111) surfaces, as well as for the intermediate H- and Cl-terminated Si surfaces. Recent measurements on Cl-terminated Si(111) surfaces have demonstrated that TIRS can be used to measure surface-associated vibrational motions in the energy region between 400 and 900 cm^{-1}, which are obscured by strong silicon crystal lattice phonon absorption in traditional multiple internal reflection infrared spectroscopy techniques.[10] Vibrational modes corresponding to Si−H and Si−Cl stretching and bending motions were used to quantify the extent of the surface functionalization after each step of a chlorination/alkylation reaction. Infrared spectroscopic characterization of the CH_3-terminated Si(111) surface has revealed the chemical structure and orientation of the methyl groups on the well-ordered surface plane. In addition, TIRS was used to probe the chemical nature of the bonds to atop Si sites for surfaces functionalized with alkyls, such as C_2H_5−, which are too large to terminate every Si atom on an unreconstructed Si(111) surface.

* To whom correspondence should be addressed.
[†] California Institute of Technology.
[‡] Rutgers University.

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II. Experimental Section

A. Materials and Methods. All solvents used in alkylation reactions were anhydrous, stored under N_2(g), and used as received from Aldrich Chemical Corp. Nanopure deionized H_2O with a resistivity of $\geq$18.2 MΩ cm was obtained from a Millipore system.

Samples were >450 μm thick, float-zone grown n-type Si(111) (Silicon Valley Microelectronics, San Jose, CA), which had been doped with phosphorus to a resistivity of >30 Ω cm. The samples were polished on both sides. Wafers were cut into rectangular samples of approximately 2 cm by 4 cm and were cleaned by sequential rinsing in a flowing stream of deionized H_2O, CH_3OH, acetone, CH_3OH, and H_2O, and were then dried with a stream of N_2(g).

To remove the native SiO_2 overlayer, the Si wafer was etched for 20 min in a solution of 40% NH_4F(aq) (Transene, Inc.) that had been degassed by bubbling with N_2(g) for at least 1 h. During the etching process, the wafers were agitated occasionally to remove bubbles that formed on the surface. After removal from the etching solution, the sample was rinsed thoroughly with H_2O and dried under a stream of N_2(g). The sample was then immediately inserted into the N_2(g)-purged TIRS sample chamber.

After TIR spectra of the H-terminated surfaces had been collected, the sample was taken into a N_2(g)-purged glovebox, and immersed in a saturated solution of PCl_5 (99.999%, Alfa Aesar) in chlorobenzene.[3] A few grains of benzoyl peroxide were added as a radical initiator, and the reaction solution was heated at 95 °C for 45 min. The sample was then removed from the reaction solution, rinsed with tetrahydrofuran (THF) and CH_3OH, and then finally rinsed again with THF, which was allowed to evaporate off the wafer. The sample was sealed in a vial under N_2(g) and taken to the IR spectrometer, where TIR spectra of the Cl-terminated surface were obtained.

To perform the surface alkylation reaction, the sample was transferred back into the N_2(g)-purged glovebox and immersed in a 1.0−3.0 M solution of $C_nH_{2n+1}MgX$, where $n = 1$ or 2, and X = Cl or Br, in THF (Aldrich).[3] Excess THF was added to the reaction solution to allow for solvent loss. The reaction was heated at 75 °C for 3 h for $n = 1$ and for 5 h for $n = 2$. At the end of the reaction, the sample was removed from the alkylmagnesium halide solution and was rinsed with copious amounts of THF and CH_3OH, then immersed in CH_3OH and removed from the N_2(g)-purged glovebox. The sample was sonicated for 5 min in CH_3OH, sonicated in acetonitrile (CH_3CN) for a further 5 min, and then dried under a stream of N_2(g). After functionalization, the sample was transferred immediately into the N_2(g)-purged sample compartment of the IR spectrometer.

B. Instrumentation. All TIR spectra were collected in the N_2(g)-purged sample chamber of a Nicolet Nexus 670 FTIR spectrometer. Spectra were recorded with use of the Omnic software package between 400 and 4000 cm^{-1} at a resolution of 4 cm^{-1} in transmission mode with a room temperature deuterated triglycine sulfate (DTGS) detector. The incident IR beam illuminated the surface at an angle, θ, of 74° off of the surface normal, i.e., at the Brewster angle for Si. At this angle, p-polarized light is transmitted through the wafer while s-polarized light is mostly reflected, preventing the use of traditional polarization experiments to determine the orientation of the observed surface vibrations. To circumvent this limitation, spectra were also recorded by illuminating the sample with an incident beam angle of 30° off of the surface normal, for which a substantial component of the electric field is parallel to the surface. An incident angle directly at the surface normal resulted in large interferences and therefore was not useful for the work described here. Probing the surface with an incident angle of 30° was primarily sensitive to modes parallel to the surface, while an incident angle of 74° was sensitive to components both parallel and perpendicular to the surface, thus providing the same information as a polarization-dependent measurement. This strategy is referred to as a "polarization-type" experiment.

After placing the sample on the angle-controlled sample holder, the chamber was closed and purged continuously with N_2(g). A spectrum was collected as the sum of 1000 consecutive scans. Five consecutive spectra were recorded in this manner, and in general, the fifth spectrum (reported herein) contained only small amounts of H_2O vapor and CO_2(g) from any remaining air introduced as the sample was placed on the sample holder. Other than use of a linear background subtraction to determine integrated areas under each peak of interest, data processing was performed without manipulation of the sample spectrum. For presentation purposes, where noted, the spectra were processed with an atmosphere background to remove any residual H_2O signal, and a linear function was used to correct the baseline for baseline fluctuations of the spectrum.

The low-energy region of the single beam spectrum of each surface was dominated by Si lattice phonon vibrations, so each sample was referenced to the surface of its precursor to subtract out common components of the signal. Thus, the H-terminated Si(111) surface was referenced to the native oxide-covered surface; the Cl-terminated surface was referenced to the H-terminated surface; and the alkyl-terminated surfaces were referenced to the Cl-terminated surfaces from which they were respectively formed. When these difference spectra are displayed in absorbance mode, positive peaks represent features that appeared during a surface reaction, while negative peaks represent chemical features that disappeared during the reaction. Features common to both of the single beam spectra, such as Si−Si phonon peaks, should cancel and appear as flat regions. Extensive experience determined that if the sample was not placed into the sample holder carefully after sequential surface modification steps, the difference spectrum contained large contributions from Si−Si phonon bands in the low-wavenumber region of the spectrum. No attempt was made to account for additional contributions to phonon absorption such as variation in the sample temperature between spectra.

Relative integrated peak areas were used to estimate the coverage of the various surface species. This required assuming that oscillator strength and orientation variations of the species under consideration underwent negligible changes between surfaces. While this critical assumption may not have always been completely accurate, it provided a useful tool for comparison between surfaces. Peak areas were estimated with the Omnic software package assuming a linear background correction.

III. Results

A. Background H- and Cl-Terminated Si(111) Surfaces. Figure 1 shows the TIR spectra of the H-terminated Si(111) surface referenced to an oxidized Si(111) reference sample at an incident IR beam angle, θ, of either 74° or 30° off of the surface normal. At an incident angle of 74°, both the Si−H stretching (ν, 2083 cm^{-1}) and bending (δ, 627 cm^{-1}) modes were clearly observed.[11−14] The Si−O−Si longitudinal optical (LO) and transverse optical (TO) motions (1224 and 1058 cm^{-1}, respectively) were seen as negative bands because they disappeared during etching of the sample in NH_4F(aq).

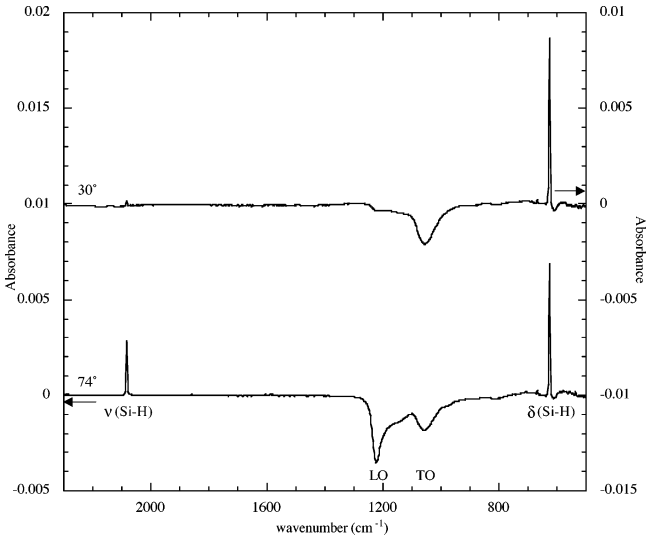

Figure 1. TIRS data and peak assignments of the H-terminated Si(111) surface. Spectra were collected at an incident beam angle of 74° (bottom) and 30° (top) off of surface normal. The spectra are on the same scale of absorbance (absorbance units), but they are offset for ease of viewing. Spectra are shown after subtraction of H_2O and flattening of the baseline.

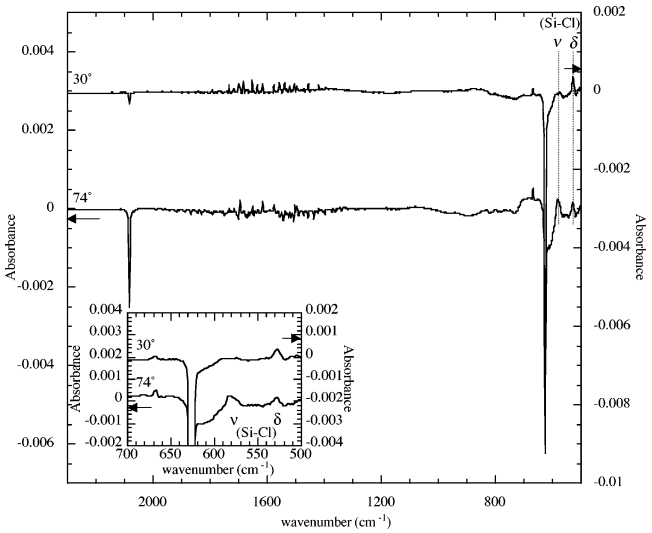

Figure 2. TIRS data and proposed peak assignments of the Cl-terminated Si(111) surface. Spectra were collected at an incident beam angle of 74° (bottom) and 30° (top) off of the surface normal. Spectra are shown after subtraction of H_2O and flattening of the baseline. The inset highlights the low-energy region of the spectrum.

As previously determined, the dependence of both modes on the incident angle is consistent with the Si−H bond being oriented perpendicular to the surface.[11] The Si−H stretching motion (2083 cm^{-1}) and the LO Si−O−Si motion (1224 cm^{-1}) decreased in intensity when the incident IR beam was moved from the Brewster angle to 30° off of the surface normal, whereas the Si−H bending (627 cm^{-1}) and the TO Si−O−Si modes (1058 cm^{-1}) displayed approximately equal intensities at both incident angles.

The vibrational modes associated with Cl-termination of Si(111) are shown in Figure 2, using the H-terminated surface as the reference. This spectrum was characterized by two peaks, at 583 and 528 cm^{-1}, with similar dependence on the incident IR beam angle to the Si−H stretching and bending mode, respectively.[15] These two modes are assigned to the Si−Cl stretching mode and to a local mode involving the parallel motion of the top silicon atom associated with the monochlorinated surface.[15,16] The negative component observed around 610 cm^{-1} was assigned to Si−Si phonon vibrational modes, and made it difficult to determine the sharpness of the Si−Cl stretching motion. The assignment of the Si−Cl stretching mode is consistent with previous high-resolution electron energy loss spectroscopy (HREELS)[3,17] and Fourier transform IR (FTIR) studies,[18−20] and both the Si−Cl stretching and bending modes have been identified by previous TIRS studies on the Cl-terminated Si(111) surface.[15,16] The assignment of these modes is also supported by the absence of any other elements on this surface other than Si, Cl, and O, as seen by both survey scan and high-resolution X-ray photoelectron spectroscopy (XPS).[7]

TABLE 1: Integrated Areas of Si−H and Si−Cl TIRS Peaks on H- and Cl-Terminated Si(111) Surfaces Assigned to Si−H and Si−Cl Vibrational Modes

		TIRS peak area (cm^{-1})	
−R	θ, deg	ν (Si−H)	δ (Si−H)
−H	74	$(1.48 \pm 0.03) \times 10^{-2}$	$(3.31 \pm 0.08) \times 10^{-2}$
	30	$(1.36 \pm 0.1) \times 10^{-3}$	$(4.2 \pm 0.2) \times 10^{-2}$
−Cl	74[a]	$(-1.45 \pm 0.07) \times 10^{-2}$	$(-3.7 \pm 0.3) \times 10^{-2}$
	30[a]	$(-1.35 \pm 0.03) \times 10^{-3}$	$(-4.4 \pm 0.6) \times 10^{-2}$

[a] Negative areas identify features on the H-terminated surface that appear as negative peaks in the difference spectrum of the Cl-terminated surface.

The relative integrated area under each peak (Table 1) was used as a qualitative measurement of the extent of surface coverage. On the freshly etched, H-terminated surface with an incident IR beam angle of 74°, the area of the Si−H stretching mode at 2083 cm^{-1} was $(1.48 \pm 0.03) \times 10^{-2}$ cm^{-1}, while the area of the bending mode at 627 cm^{-1} was $(3.31 \pm 0.08) \times 10^{-2}$ cm^{-1}. When this surface was chlorinated, the area of the negative Si−H stretching peak in the difference spectrum, attributed to Si−H bonds that had been removed from the surface by the chlorination reaction, was $(-1.45 \pm 0.07) \times 10^{-2}$ cm^{-1}. The corresponding value for the Si−H bending motion at 627 cm^{-1} on this surface was $(-3.7 \pm 0.3) \times 10^{-2}$ cm^{-1}. Within the error of the experiment and the area determination technique, the same relative amount of Si−H present on the freshly etched surface disappeared on the Cl-terminated surface, supporting the hypothesis that Si−H species on the freshly etched surface are quantitatively replaced by Si−Cl species when the surface is exposed to the PCl_5 solution, in agreement with previous XPS observations.[7] The integrated areas of both Si−H vibrational modes when scanned at an incident IR beam angle of 30°, given in Table 1, confirm these observations, in accord with the behavior of surfaces prepared by a gas-phase chlorination method.[15]

B. CH_3-Terminated Si(111) Surfaces. Figure 3 shows the TIRS spectra of a CH_3-terminated Si(111) surface that had been prepared by treating the Cl-terminated surface with CH_3MgX. Because these spectra are referenced to the Cl-terminated Si(111) sample, negative peaks in the absorption spectrum represent features of the Cl-terminated surface that disappeared during the alkylation reaction. On the Cl-terminated Si surfaces shown in Figure 2, the integrated areas of the Si−Cl stretching and bending modes at 583 and 528 cm^{-1}, respectively, when examined at an IR incident angle of 74°, were $(1.0 \pm 0.6) \times 10^{-2}$ and $(3.7 \pm 0.9) \times 10^{-3}$ cm^{-1}, respectively (Table 2). Similar areas were observed at the same incident angle for the corresponding negative Si−Cl features in the spectra of the CH_3-terminated surface (Figure 3, Table 2). At an incident angle of 30°, the measured integrated areas under the Si−Cl bending mode at 528 cm^{-1} were also similar for the Cl-terminated (positive peak, Figure 2) and CH_3-terminated (negative peak,

TABLE 2: Integrated Areas of TIRS Peaks on Cl- and CH_3-Terminated Si(111) Surfaces Assigned to Si−Cl and C−H Vibrational Modes

		TIRS peak area (cm^{-1})			
−R	θ, deg	ν(Si−Cl)	δ(Si−Cl)	δ_s(C−H)	ρ(C−H)
−Cl	74	$(1.0 \pm 0.6) \times 10^{-2}$	$(3.7 \pm 0.9) \times 10^{-3}$		
	30		$(3.8 \pm 0.6) \times 10^{-3}$		
$-CH_3$	74[a]	$(-7 \pm 2) \times 10^{-3}$	$(-2.3 \pm 0.01) \times 10^{-3}$	$(2.2 \pm 0.2) \times 10^{-3}$	$(1.8 \pm 0.2) \times 10^{-2}$
	30[a]		$(-2.8 \pm 1.6) \times 10^{-3}$		$(1.7 \pm 0.3) \times 10^{-2}$
$-C_2H_5$	74[a]	$(-5 \pm 1) \times 10^{-3}$	$(-3 \pm 1) \times 10^{-3}$		
	30[a]		$(-3.6 \pm 0.5) \times 10^{-3}$		

[a] Negative areas identify features on the H-terminated surface that appear as negative peaks in the difference spectrum of the Cl-terminated surface.

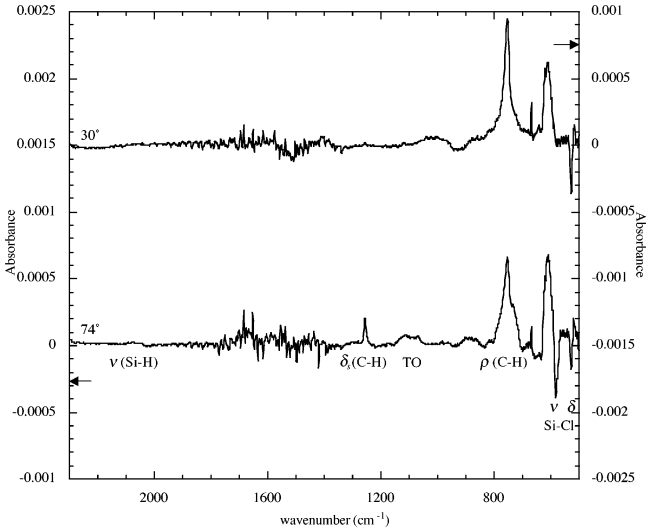

Figure 3. TIRS data and proposed peak assignments of the CH_3-terminated Si(111) surface. Spectra were collected at an incident beam angle of 74° (bottom) and 30° (top) off of the surface normal. Spectra are shown after subtraction of H_2O and flattening of the baseline.

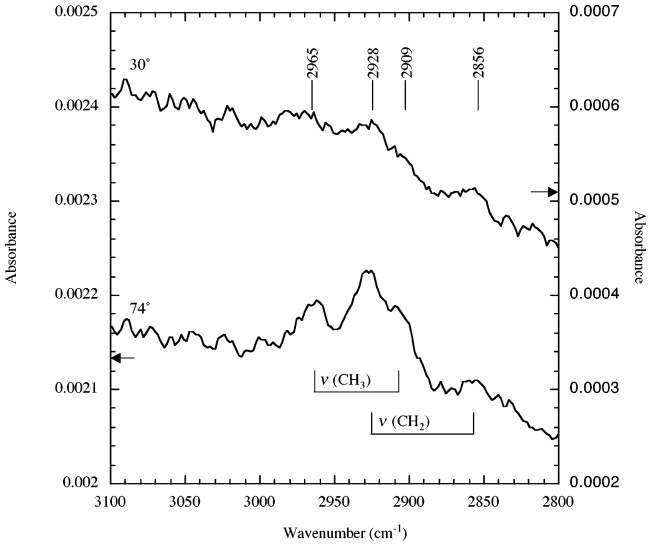

Figure 4. TIRS data and proposed peak assignments of the C−H stretching region of the CH_3-terminated Si(111) surface. Positions of relevant peaks are noted above the spectra. The raw spectra are shown with no alteration, such as background smoothing, but are offset for clarity.

Figure 3) Si(111) surfaces. This behavior indicates that all of the TIRS-observable Si−Cl bonds initially present on the surface have been removed during the alkylation reaction, in agreement with previous XPS observations of this surface.[7]

On the CH_3-terminated Si surface shown in Figure 3, a small, broad peak centered near 2070 cm^{-1} was observed when TIRS was collected at an incident IR beam angle of 74° off surface normal. The integrated area of this peak was <10% of the surface coverage of the freshly etched H-terminated Si(111) surface reported in Table 1. This could represent a small amount of surface Si−H contamination present on the freshly methylated surface, although no further experiments were done to determine the origin of this signal. A large Si−Si phonon mode, which can be seen in Figure 3, appeared to have a shoulder at 620 cm^{-1}. This is significantly below the energy of the Si−H bending motion and it was not possible to confirm that the signal at 2068 cm^{-1} represented surface Si−H groups.

The CH_3-terminated Si(111) surface also exhibited distinct peaks in the C−H stretching region at approximately 2900 cm^{-1} (Figure 4). Vibrational absorption features at 2856, 2909, 2928, and possibly 2965 cm^{-1} were observed when the spectra were collected at an incident IR beam angle of 74°, but all of these features were reduced in intensity when the incident IR beam angle was 30° (Figure 4). From simple group theory considerations, a CH_3^- group should have two IR-active vibrational modes, an a_1 symmetric stretching mode and an e asymmetric stretching mode at slightly higher wavenumber.[21] Previous investigations of CH_3-terminated porous Si structures, with an amorphous surface structure but high surface IR signal, have observed broad C−H symmetric and asymmetric stretches centered at ~2900 and 2970 cm^{-1}, respectively.[22] FTIR studies of silicon oxide surfaces terminated with trimethylsilane have revealed methyl C−H stretches at 2904 and 2963 cm^{-1}.[23] Peaks at 2909 and 2965 cm^{-1} thus would be consistent with expected positions for the methyl C−H symmetric and asymmetric stretching vibrations, respectively. A possible assignment of the peaks at 2856 and 2928 cm^{-1} can be made noting that porous Si alkylated with a 6-trifluoroacetamindohexyl group, in which all of the C−H bonds arise from methylene (CH_2) groups, exhibits C−H stretching modes at 2860 and 2936 cm^{-1},[24,25] and thus the peaks at 2856 and 2928 cm^{-1} would arise from adventitious hydrocarbons adsorbed on the surface as a result of the chemical treatments used in the alkylation process.

The low-wavenumber region of vibrational absorptions on the CH_3−Si(111) surface collected with two different incident IR beam angles, along with proposed peak assignments, is shown in Figure 3. When the surface was examined with the IR beam incident at the Brewster angle ($\theta = 74°$), a sharp feature at 1257 cm^{-1} was clearly visible, but this peak disappeared at $\theta = 30°$, indicating a mode polarized perpendicular to the surface. This peak was assigned as the C−H symmetric bending, or "umbrella", mode of the methyl group.[22,27] This mode is expected to be normal to the surface if CH_3 replaces Cl on Si(111) as shown in Chart 1.

A second sharp peak at 757 cm^{-1} appeared at both data collection angles. This absorption energy is expected for a methyl C−H rocking mode,[27] which would be polarized parallel

to the surface if it originated from a methyl group oriented normal to the Si(111) surface plane. Observation of this mode therefore is expected even when the incident IR beam is itself near the surface normal. The integrated areas of both of these peaks at both data collection angles are given in Table 2.

Another feature present in the spectrum shown in Figure 3 when collected at $\theta = 74°$ was a small, broad absorption near 1100 cm^{-1}, corresponding possibly to the TO mode of Si−O−Si. Interestingly, this feature was not observed for $\theta = 30°$, in contrast to expectations for a typical TO phonon mode (see for instance Figure 1). The spectra at the two different beam angles displayed in Figure 3 were collected on two different samples, so appearance of the TO peak on one sample could possibly have been caused by small variations in the amount of O incorporated in the near-surface Si lattice. The amount of oxide on the surface was estimated by assuming that the native silicon oxide was 15 Å thick, and determining the ratio of the integrated areas of the TO peak on the CH_3-terminated surface to that observed for the native oxide surface (negative peak in Figure 1). The TO peak on the CH_3-terminated surface corresponded to a possible Si−O−Si coverage of 0.03 monolayers (ML), or approximately 0.5 Å of equivalent Si−O−Si thickness. Previous TIRS investigations on the intermediate, Cl-terminated, Si(111) surface have demonstrated that a small amount of subsurface oxide (∼0.5 Å average) is introduced through the chlorination of the H-terminated surface giving a total average oxide thickness of ∼1 Å.[16]

In the low-energy region of the TIR spectrum, a feature at ∼730 cm^{-1} was observed as a large shoulder on the C−H rocking motion when data were collected at the Brewster angle, but disappeared when the incident angle of the IR beam was moved toward the surface normal (Figure 3). This polarization-type behavior suggested that the mode could be a Si−C surface motion oriented perpendicular to the Si(111) surface plane, although this peak position would be higher in energy than most proposed Si−C stretches on alkylated Si(111) surfaces observed previously with HREELS.[28−33] Finally, Figure 3 shows a broad feature at ∼620 cm^{-1} at both data collection angles. This mode corresponded to a Si−Si lattice phonon mode that was not perfectly subtracted from the CH_3-terminated surface by referencing with the Cl-terminated surface.[34] The residual signal may possibly result from a slight difference in the placement of the two surfaces in the FTIR sample holder or from a small temperature variation during data collection.[34] A sharp absorption at 667 cm^{-1} was also observed from atmospheric CO_2(g) contamination in the FTIR sample compartment, and scaled with the corresponding CO_2(g) stretching modes at ∼2300 cm^{-1}.

C. C_2H_5-Terminated Si(111) Surfaces. TIRS data were also collected on a Cl-terminated surface that had been exposed to a solution of ethylmagnesium halide. Figure 5 shows the TIR spectra of the C_2H_5-terminated surface, and Figure 6 shows an expansion of the low-energy region of these spectra. The negative peaks at 583 and 528 cm^{-1} corresponded to the Si−Cl stretching and bending modes, respectively, that were lost during the ethylation reaction. As on the CH_3-terminated Si surface, the integrated areas of the Si−Cl bending and stretching peaks were used to determine the extent of replacement of the Si−Cl bonds by the alkylation process. The integrated area of the positive feature on the Cl-terminated surface at 528 cm^{-1} was identical, within the error of the experiment, to that of the negative feature on the C_2H_5-terminated surface (Table 2). This observation supports previous XPS observations that all Cl is removed from the Si surface during exposure to the alkylmagnesium halide solution, even for functional groups in which

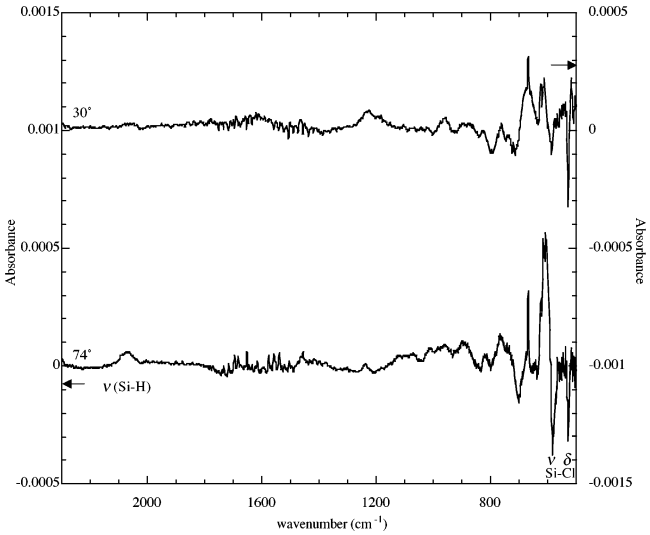

Figure 5. TIR spectra and proposed peak assignments of the C_2H_5-terminated Si(111) surface. Spectra are shown after subtraction of H_2O and flattening of the baseline.

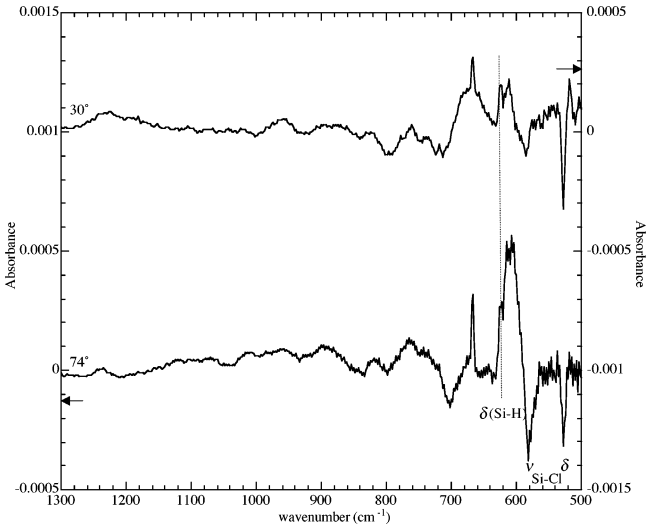

Figure 6. TIRS data and proposed peak assignments of the low-energy region of the C_2H_5-terminated Si(111) surface. Spectra are shown after subtraction of H_2O and flattening of the baseline.

not all atop Si(111) atoms can be bonded to the alkyl moiety because of the steric bulk of the alkyl group.[7] The data from the Si−Cl stretching mode (583 cm^{-1}) were not as conclusive, although measurement of the area under this peak could have been hampered by interference from the Si−Si phonon region directly above 600 cm^{-1}.

On the C_2H_5-terminted Si(111) surface, a broad peak centered at approximately 2070 cm^{-1} was observed when the TIRS data were collected with an incident IR beam angle of 74° off of surface normal, but this peak was not observed when the data collection angle was reduced to 30° (Figure 5). This peak position is near the energy of the peak representing the Si−H stretching motion (2083 cm^{-1}) observed in the spectrum of the freshly etched H-terminated Si(111) surface (Figure 1). This broad peak could therefore correspond to surface Si−H atoms present on the surface after the alkylation, consistent with the hypothesis that if Si−Cl termination has been fully eliminated by the C_2H_5MgX treatment, the nonalkylated Si atop sites could be terminated with Si−H bonds.[7] For isolated Si−H modes on Si(111), the absorption is expected to be at lower frequency due to the removal of dipole interactions, and broad due to the

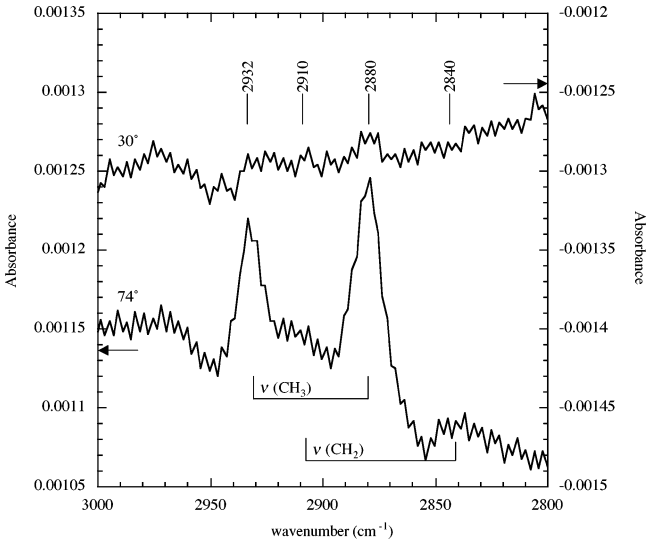

Figure 7. TIRS data and proposed peak assignments of the C−H stretching region of C_2H_5-terminated Si(111). The spectra are shown before any data manipulation was conducted.

variation in the chemical environment. The area under this peak corresponded to a coverage of surface Si−H bonds of 14% of the freshly etched surface, indicating that a substantial portion of atop Si atoms are bonded to ethyl groups, and that only a small amount of the surface is terminated with H groups. Extensive work is ongoing in our laboratory to quantify further the full coverage of ethyl groups on the (111) surface, and to determine how an alkyl group with a van der Waals diameter of 5.4−5.0 Å[35,36] can pack to such high extent on a surface with an internuclear Si atop site distance of 3.8 Å.[37]

Upon close inspection of the low-wavenumber region of this surface, a feature at 627 cm^{-1} was apparent at both IR beam incident angles (Figure 6). This peak may correspond to the Si−H bending vibrational feature at ∼2070 cm^{-1}, but the shape and size of this peak were difficult to determine because the peak was partly buried by a strong Si−Si phonon mode at ∼610 cm^{-1}. This Si−H feature would be expected for a mixed surface monolayer comprised partly of Si−H and partly of Si−C bonds, again consistent with the hypothesis that the C_2H_5-terminated Si(111) surface is covered to some extent with Si−H bonds after the two-step chlorination/alkylation procedure.[7] The only other peak seen in this energy region was a sharp absorption feature at 667 cm^{-1} arising from the presence of CO_2(g) in the spectrometer. Neither the CH_3-symmetrical bending (1250 cm^{-1}) nor the C−C stretching (1000−1050 cm^{-1}) vibrational modes were observed on the C_2H_5-terminated Si surface.

Figure 7 shows the C−H stretching region near 2900 cm^{-1}, revealing vibrational absorptions at 2840, 2880, 2910, and 2932 cm^{-1} when the IR beam was 74° off of the surface normal. Previous FTIR observations of ethyl groups on Si(111) surfaces have been limited in scope,[38,39] but ZnO and ZrO_2 surfaces have been ethylated, and vibrational absorption features with four distinct peaks have been observed.[40,41] On the basis of these previous observations, as well as on FTIR data of self-assembled alkylthiol monolayers on gold,[25] C−H stretching vibrational modes for the C_2H_5-terminated Si(111) surface would be expected at 2840 and 2910 cm^{-1} arising from the CH_2 methylene unit, and peaks at 2880 and 2932 cm^{-1} would be expected due to the CH_3 methyl group. Table 3 summarizes the surface vibrational peaks observed on all of the functionalized surfaces measured in this work.

TABLE 3: Assignment of TIRS Peaks Observed on Functionalized Si(111) Surfaces

	TIRS peak location			
−R	ν (cm^{-1})	intensity[a]	assignment	⊥ to surface?
−H	2083	s	ν(Si−H)	yes
	627	s	δ(Si−H)	no
−Cl	583	m	ν(Si−H)	yes
	528	m	δ(Si−H)	no
$-CH_3$	2965	m	$\nu_a(C-H)_{CH_3}$	
	2928	s	$\nu_a(C-H)_{CH_2}$	
	2909	m	$\nu_s(C-H)_{CH_3}$	
	2856	w	$\nu_s(C-H)_{CH_2}$	
	1257	m	$\delta_s(C-H)_{CH_3}$	yes
	1100	w	TO (Si−O−Si)	
	757	s	$\rho(C-H)_{CH_3}$	no
$-C_2H_5$	2932	s	$\nu_a(C-H)_{CH_3}$	
	2910	m	$\nu_a(C-H)_{CH_2}$	
	2880	s	$\nu_s(C-H)_{CH_3}$	
	2840	w	$\nu_s(C-H)_{CH_2}$	
	2080	m	ν(Si−H)	yes
	627	m	δ(Si−H)	no

[a] Qualitative assessment of peak intensity: s = strong, m = medium, w = weak.

IV. Discussion

Comparing the TIR spectrum of a freshly prepared Cl-terminated Si(111) surface referenced against a H−Si(111) sample to the TIR spectrum of that H-terminated surface referenced to an oxide-covered Si sample revealed that all surface Si−H bonds had been removed, consistent with the hypothesis that chlorination by PCl_5 quantitatively replaces surface Si−H bonds with Si−Cl bonds to form the monochlorinated surface. Furthermore, the small full width at half-maximum (fwhm) of the Si−Cl stretching and bending modes on the Cl-terminated Si(111) sample indicated that this surface was highly homogeneous. Because the Cl-terminated surfaces were made from an atomically flat, H-terminated Si surface, this high homogeneity indicates that PCl_5 chlorination of the H−Si(111) sample does not lead to extensive roughening or pitting of the surface.[16,42]

When this monochlorinated surface was exposed to an alkylmagnesium halide solution, the Si−Cl stretching and bending peaks were used to determine the extent of removal of Si−Cl bonds by the alkylating reagent. Within the detection limit of the instrument and the accuracy of the measurement technique, the Si−Cl species were completely removed during exposure to the alkylmagnesium halide reagent. Although the surface modification procedure was conducted under rigorously O_2- and H_2O-free conditions to avoid oxidizing the Si surface, occasionally TIRS evidence for Si−O−Si vibrational modes was observed near 1100 cm^{-1}. Any such oxides were present, however, in amounts corresponding to an equivalent monolayer thickness of <1 Å. This conclusion is supported by extensive high-resolution XPS results on the freshly prepared alkyl-terminated Si(111) surface, which have demonstrated that the two-step chlorination/alkylation functionalization route generates surfaces free of any significant quantity of silicon oxide species.[7,9]

The observation of the surface Si−C stretching mode is less clear. Previous HREELS experiments have located that mode between 600 and 700 cm^{-1}. In the experiments presented here, no conclusive evidence of a Si−C vibrational mode was observed, mostly because of the difficulty in eliminating unwanted Si phonon absorption in the vicinity of 600−650 cm^{-1}. On the CH_3-terminated surface, two regions were examined carefully for evidence of the Si−C stretch. The first

was ~730 cm^{-1}, where a broad shoulder on the C−H rocking mode appeared at an incident IR beam angle of 74°, but disappeared when the IR beam was moved to an incident angle of 30°. This is representative of a surface-associated vibrational mode that is oriented perpendicular to the Si surface, as seen for example in the Si−Cl and Si−H stretching motions at 583 and 2083 cm^{-1}, respectively. However, HREELS investigations have placed the Si−C stretching vibration below 700 cm^{-1},[28−33] much lower in energy than the peak observed here at 730 cm^{-1}.

The second absorption region that was investigated closely was the area between 600 and 620 cm^{-1}, which was often obscured by a large Si−Si phonon vibration that was particularly difficult to reduce in the difference spectrum. To subtract this feature out of the difference spectrum appropriately, TIR spectra of a SiO_2-covered Si wafer were recorded at an incident beam angle of 74°and 73°. Because the surface was deliberately offset in the sample holder, when the difference spectrum of these two samples was calculated, it consisted of a large Si−Si phonon vibration covering the 600−620 cm^{-1} region. This signal was then used as a background spectrum, which was subtracted from the difference spectrum of the CH_3-terminated Si(111) surface. If the Si−Si phonon background is subtracted correctly, any feature remaining under that region should be uncovered after the subtraction is completed. This procedure, however, revealed nothing on the CH_3-terminated surface, even after the Si−Si lattice phonon appeared to be completely accounted for (data not shown). Given the demonstrated sensitivity to vibrational absorptions in this region, particularly for ν and δ (Si−Cl), the lack of any clear signal that can be definitely attributed to the surface Si−C stretching mode in this region warrants further investigation.

For bulkier substituents, given the reactants that the Si(111) surface is exposed to during surface functionalization, Si termination by H, O, Cl, or Mg is possible in principle for sites that are not terminated by alkyl groups. Previous investigations on the C_2H_5-terminated Si(111) surfaces by high-resolution core photoelectron spectroscopy techniques observed, to the detection limits, no Si−O or Si−Cl bonds, nor any residual Mg remaining on the functionalized surface.[1,7] By elimination, the XPS spectra therefore suggest that H atoms might be bonded to surface Si atoms that are not bonded to ethyl groups.[7] The TIRS results presented herein, which reveal a broad absorption centered at 2070 cm^{-1} assigned to the Si−H stretching motion, and a sharp peak at 627 cm^{-1} assigned to the Si−H bending motion, suggest that hydrogen atoms are bonded to the nonalkylated surface Si atoms. The unusually broad Si−H stretching motion indicates that the surface Si−H bonds are in a variety of different chemical environments, as expected for a surface bonded to bulky alkyl groups which will be substantially less ordered than the ideal, freshly etched H-terminated Si(111) surface.

The position of the methylene C−H stretching modes on the C_2H_5-terminated surface can be related to the packing order of longer surface-bound alkyl chains.[43−45] A shift to lower energy has been taken to indicate increased order in the overlayer, reflecting a crystalline-like layer as opposed to a liquid-like structure. The positions of the methylene C−H symmetric and asymmetric stretching modes at 2840 and 2910 cm^{-1}, respectively, place them somewhat lower in energy than signals on Au surfaces having alkanethiols of greater than 5 carbon atoms (~2850 and 2920 cm^{-1}, respectively),[44] but slightly higher in energy than peaks observed for diethyl zinc overlayers on ZrO_2 (2813 and 2904 cm^{-1}, respectively).[41] It is difficult to compare the ethyl group to a crystalline- or liquid-like state, but it appears that when compared to previously studied hydrocarbon overlayers, the C_2H_5-terminated Si(111) surface is fairly well-ordered and closely packed.

V. Conclusions

TIRS data on H- and Cl-terminated Si(111) surfaces have confirmed that Si−H bonds on the freshly etched Si surface are replaced with Si−Cl bonds upon exposure to PCl_5 and a radical-generating reagent. Polarization-type studies of the Si−Cl stretching and bending modes at 583 and 526 cm^{-1}, respectively, support the conclusion from SXPS studies that the Cl-terminated surface is monochlorinated. The CH_3 symmetric bending or "umbrella" mode at 1257 cm^{-1} was observed and the methyl-terminated surface and was found to be oriented perpendicular to the surface plane, consistent with the expectations for a surface-bound methyl group defined by the tetrahedral geometry of both the (111) surface Si atoms and the methyl carbon atom. On the ethyl-terminated surface, although the bulky alkyl group cannot terminate every Si atop atom, all Cl was removed from the surface by immersion in the ethylmagnesium halide reagent. The presence of a broad, perturbed Si−H stretching motion at ~2070 cm^{-1} and an Si−H bending motion at 627 cm^{-1} indicated that any unalkylated Si surface atoms were terminated with H atoms introduced to the sample either during the alkylation reaction or as it is exposed to the solvents used in rinsing and cleaning the sample after exposure to the alkylating solution.

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