

Low-Temperature STM Images of Methyl-Terminated Si(111) Surfaces

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Low-temperature scanning tunneling microscopy (STM) has been used to image CH₃-terminated Si(111) surfaces that were prepared through a chlorination/alkylation procedure. The STM data revealed a well-ordered structure commensurate with the atop sites of an unreconstructed 1 × 1 overlayer on the silicon (111) surface. Images collected at 4.7 K revealed bright spots, separated by 0.18 ± 0.01 nm, which are assigned to adjacent H atoms on the same methyl group. The C–H bonds in each methyl group were observed to be rotated by 7 ± 3° away from the center of an adjacent methyl group and toward an underlying Si atom. Hence, the predominant interaction that determines the surface structure arises from repulsions between hydrogen atoms on neighboring methyl groups, and secondary interactions unique to the surface are also evident.

Hydrogen-terminated (111)-oriented Si surfaces are well documented to have a low number of structural and electrically active defect sites.^{1,2} However, these surfaces degrade rapidly in air and in other oxidizing environments.^{3,4} Consequently, several wet chemical methods have been developed for the functionalization of both crystalline and porous Si surfaces.^{5–10} These chemical methods offer molecular-level control over the interfacial chemistry of Si surfaces, attracting attention for applications in molecular electronics,¹¹ sensing,^{12–14} photoelectrochemistry,⁴ chemical and electrical surface passivation,^{8,15} porous Si photoluminescence,⁹ and control of photopatterning.⁶

Molecular modeling indicates that methyl groups are the only saturated hydrocarbon moiety that can terminate every Si atop site on the unreconstructed Si(111) surface.^{8,16–17} Such complete chemical termination is expected to offer the most robust passivation of surface defects and to provide the best resistance to oxidation of the resulting Si surfaces. Prior workers have hypothesized that functionalization with longer alkyl chains yields incomplete coverage of the Si(111) surface,¹⁸ with the remainder of the sites being terminated by either –OH, –H, or other unidentified surface species.^{16,19} In this work, we report low-temperature STM studies that have revealed the structure of the fully methyl-terminated Si(111) surface prepared by wet chemical methods.

Silicon surfaces were functionalized using a two-step chlorination/alkylation procedure.⁸ The samples were obtained from (111)-oriented, Sb-doped, 0.005–0.02 Ω cm resistivity, n-type Si wafers having a miscut error of ±0.5°. The samples were cleaned and oxidized for 5 min at 80 °C in a solution of 1:1:5

(vol) 30% H₂O₂/30% NH₃/H₂O and were then terminated with Si–H bonds by etching for 15 min in 40% NH₄F(aq). This etching method has been demonstrated to produce large atomically flat terraces.²⁰ Chlorination was performed by exposing the samples to a solution of PCl₅ in chlorobenzene.⁸ A small amount of benzoyl peroxide was added to initiate a radical reaction, and the samples were heated to 90–100 °C for 45 min. The surfaces were removed from solution, rinsed with tetrahydrofuran (THF) and CH₃OH, and then dried under a stream of N₂(g). The resulting Cl-terminated surfaces were exposed for 3 h to a solution of 3.0 M CH₃MgCl in refluxing THF.⁸ The samples were then rinsed with THF and CH₃OH, followed by sonication in CH₃OH and CH₃CN each for 5 min. The samples were dried under a stream of N₂(g), mounted onto a sample stage, and quickly introduced into the ultrahigh vacuum (UHV) system of the STM. STM data of the resulting surfaces were obtained in an Omicron low-temperature UHV STM using etched or mechanically cut Pt/Ir STM tips.

Prior work has indicated that surfaces prepared through this two-step wet chemical procedure exhibit no detectable chlorine or silicon oxide in surface-sensitive X-ray photoelectron spectroscopy experiments and resist oxidation by air or aqueous solutions.^{4,8,15} Infrared spectroscopy indicates that such surfaces have covalent Si–C bonds.²¹ For CH₃-terminated Si surfaces prepared in a similar manner, photoelectron diffraction has been used to estimate the length of the Si–C bond as 0.18 nm.¹⁶ Very recent STM data on CH₃-terminated Si surfaces have revealed bright spots in an unreconstructed (1 × 1) adlattice structure on the Si surface.²²

Figure 1 compares STM images of the morphology of the H-terminated Si(111) surface with that of the CH₃-terminated surface. A slight increase in the etch pit density was observed

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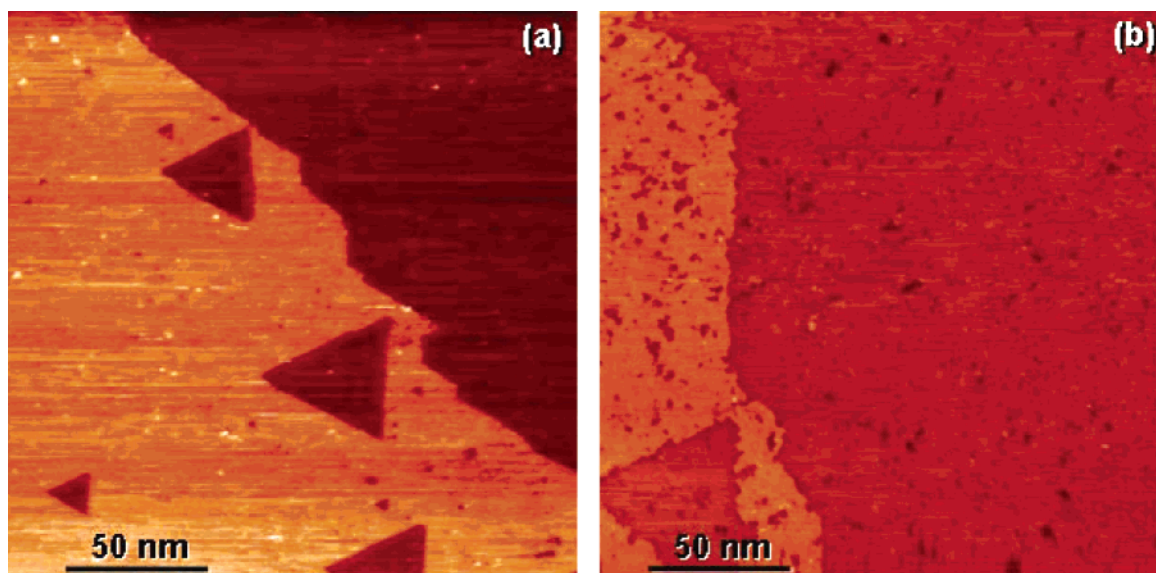


Figure 1. STM images of (a) H-terminated and (b) CH₃-terminated Si(111) surfaces. Both 200 nm \times 200 nm images, taken at 77 K, show large flat terraces separated in height by single atomic steps. The triangular etch pit orientation was unaffected by the two-step alkylation procedure.

as a result of the chlorination/alkylation procedure, but large flat terraces, separated in height by single atomic steps, were observed on both types of surfaces.

Figure 2 shows STM images of the CH₃-terminated surface at 77 and 4.7 K, respectively. The image at 77 K (Figure 2a, inset) consisted of a series of triangularly shaped bright regions in a 1×1 structure, with the spots separated by a distance of 0.38 ± 0.01 nm. This distance is equal to the spacing between atop sites on an unreconstructed Si(111) surface. The ordering was quite robust, with relatively few defects observed over large regions of the surface.

STM data at 4.7 K (Figure 2a) revealed further structure in the CH₃-terminated surface, with the triangularly shaped regions each resolved into three spots separated from each other by an average distance of 0.18 ± 0.01 nm. The 0.18-nm distance is consistent with the distance between hydrogen atoms in an sp³-hybridized methyl group.

The repulsions between H atoms on adjacent $-\text{CH}_3$ groups would be minimized if the C–H bonds on a methyl group were oriented directly toward the carbon atoms on adjacent $-\text{CH}_3$ groups (i.e., if $\angle \text{A–B–C} = 0$ in Figure 2a). However, the STM data of Figure 2a indicated that the C–H bonds were rotated by $7 \pm 3^\circ$ away from the center of the neighboring $-\text{CH}_3$ group (angle $\text{A–B–C} = 7^\circ$ in Figure 2a).

The orientation of this rotation relative to the location of the underlying Si–Si bonds requires registry of the overlayer structure with that of the underlying Si lattice. The manufacturer indicated that the flat supplied with the Si wafer was cut along the $[1\bar{1}0]$ direction, and this conclusion was independently verified by X-ray diffraction measurements on these Si samples. The physical orientation of the Si samples was controlled during the steps of wafer dicing and sample placement in the STM instrument so that the directions of the low-index planes of the Si crystal were precisely known, and are indicated in Figure 2a.

The Si lattice orientation on such samples was furthermore independently verified by an analysis of the orientation of the triangular etch pits, such as those at the lower left corner of Figure 1b, observed in STM images of the mounted sample. The step edges of such pits on H-terminated Si(111) have been identified as the $\langle 11\bar{2} \rangle$ family, with termination by Si mono-

hydride groups.²³ STM studies indicated that the step edges on such pits in the H-terminated Si (111) surface did not change orientation as a result of the two-step alkylation/chlorination process. The orientation of the pits in Figure 1b therefore provided independent confirmation of the direction of the low-index lattice planes.

Consistent with prior photoelectron diffraction studies,¹⁶ the topmost Si atoms are assumed to be located directly below the center of the each triangular cluster of (methyl-derived) bright spots in the STM image. The resulting orientation of the Si unit cell relative to the STM bright spots of the sample is indicated by the parallelogram in Figure 2a. Figure 3 presents a model for the structure of the CH₃-terminated surface that is consistent with the STM and crystal orientation data. This analysis indicates that the C–H bonds in the overlayer are rotated slightly toward the nearest Si–Si bonds in the underlying Si crystal, producing an angle A–B–D in Figure 3 of 23° .

Small organic molecules such as $\text{H}_3\text{C–CH}_3$, $\text{H}_3\text{C–SiH}_3$, $\text{H}_3\text{–Si–SiH}_3$, $\text{CH}_3\text{–C}(\text{CH}_3)_3$, and $\text{SiH}_3\text{–Si}(\text{SiH}_3)_3$ prefer the staggered conformation (by 2.68, 1.40, 0.94, 3.66, and 0.73 kcal/mol, respectively, at the B3LYP level with a 6311G**++ basis set). This type of interaction would be expected to yield an angle A–B–D of 60° for an isolated methyl group bonded to a (111) Si surface. In contrast, repulsions between adjacent methyl groups in the overlayer clearly dominate the interactions on a fully covered CH₃-terminated Si surface structure. The minimization of such repulsions would produce an A–B–D angle of 30° , close to the 23° angle deduced from the STM data. A secondary effect, manifested by a favorable interaction that produces an A–B–D angle of 23° on the methyl-terminated Si surface (as opposed to a repulsion between C–H methyl bonds and the Si–Si bonds leading from the Si bonded to the methyl group, which would be expected to produce an angle $\text{A–B–D} > 30^\circ$) is the subject of extensive theoretical analysis in our laboratory.

Molecular mechanics calculations were also performed in which the Si–C bond length was artificially increased to 1.0 nm to minimize interactions between the C–H and Si–Si bonds. The minimum-energy structure for such a surface was calculated to have an A–B–D angle of 30° , providing further confirmation

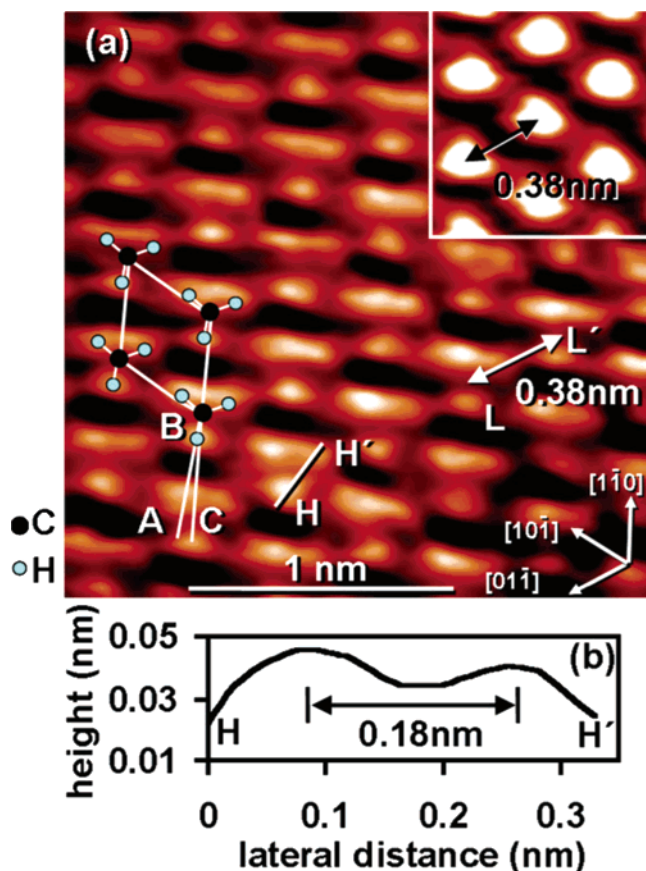


Figure 2. (a) STM image of methyl-terminated Si(111), collected at 4.7 K, at a sample bias of $V_s = -2.5$ V and at a constant current of 0.050 nA. The color range (dark = low; bright = high) is 0.05 nm. The separation between the centers of the three bright spots, marked as line L–L', is 0.38 nm. The directions of the low-index planes of this crystal, as determined from X-ray crystallography, are indicated in the lower right. The drawn parallelogram represents the surface unit cell. Four methyl group drawings are superimposed onto the image, assuming that the methyl groups are in registry with atop Si atoms, to illustrate the position and relative orientation of methyl groups. The angle formed between A, B, and C is $7 \pm 3^\circ$. (Inset) STM image, taken at 77 K on the same methylated Si(111) surface, revealing a series of triangularly shaped bright regions in a 1×1 structure, with the spots separated by a distance of 0.38 ± 0.01 nm. Image size: 1 nm \times 1 nm. No detailed structure in the bright spots was observed at this temperature. (b) A profile of the line marked as H–H' in part a. The distance between the centers of the two maxima on the line is 0.18 nm, which is the expected distance between adjacent H atoms on the same methyl group.

that the interactions that determine the packing of the CH_3 -terminated Si surface are primarily the repulsions between hydrogen atoms on adjacent methyl groups in the functionalized organic overlayer, tempered by an attractive preference for the eclipsed conformation relative to the underlying Si–Si bonds.

In summary, the two-step chlorination/alkylation process produced a highly ordered CH_3 -terminated Si(111) surface with very few structural defects. The methyl groups were frozen into discrete structural positions at 4.7 K, with the packing dominated by repulsive interactions between hydrogen atoms on adjacent methyl groups in the organic overlayer. The data attest to the high degree of structural perfection obtainable on methylated Si surfaces that are produced through simple wet chemical methods. The structural perfection suggests that these surfaces can provide superior properties in many electrical and chemical

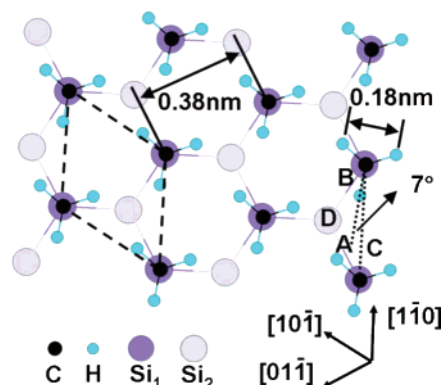


Figure 3. Proposed structural model of the methyl-terminated Si(111) surface. Crystallographic orientations are shown, and the $-\text{CH}_3$ groups are viewed along the $[111]$ direction. A unit cell is outlined by the parallelogram. Top silicon atoms that are directly bonded to the methyl groups are labeled as Si_1 , and silicon atoms in the layer below the atop sites are labeled as Si_2 . Given the measured angle A–B–C of $7 \pm 3^\circ$ and registering the unit cell atoms under the methyl groups indicate that the angle between a C–H bond and the adjacent Si–Si bond, with both bonds projected onto the (111) plane, defined by A–B–D, is $23 \pm 3^\circ$.

applications where the H-terminated Si is too unstable to be used for extended time periods or for which organic functionalization is needed to impart desired chemical properties to the Si surface.

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