

Chemical and electronic characterization of methyl-terminated Si(111) surfaces by high-resolution synchrotron photoelectron spectroscopy

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The chemical state, electronic properties, and geometric structure of methyl-terminated Si(111) surfaces prepared using a two-step chlorination/alkylation process were investigated using high-resolution synchrotron photoelectron spectroscopy and low-energy electron diffraction methods. The electron diffraction data indicated that the methylated Si surfaces maintained a (1×1) structure, where the dangling bonds of the silicon surface atoms were terminated by methyl groups. The surfaces were stable to annealing at 720 K. The high degree of ordering was reflected in a well-resolved vibrational fine structure of the carbon $1s$ photoelectron emission, with the fine structure arising from the excitation of C-H stretching vibrations having $h\nu = 0.38 \pm 0.01$ eV. The carbon-bonded surface Si atoms exhibited a well-defined x-ray photoelectron signal having a core level shift of 0.30 ± 0.01 eV relative to bulk Si. Electronically, the Si surface was close to the flat-band condition. The methyl termination produced a surface dipole of -0.4 eV. Surface states related to π_{CH_3} and $\sigma_{\text{Si-C}}$ bonding orbitals were identified at binding energies of 7.7 and 5.4 eV, respectively. Nearly ideal passivation of Si(111) surfaces can thus be achieved by methyl termination using the two-step chlorination/alkylation process.

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I. INTRODUCTION

The functionalization of semiconductor surfaces, particularly silicon, with organic moieties is a promising development in producing new semiconductor-based materials and devices. Covalent attachment of organic species either by wet chemical or vacuum-based dry preparation methods provides new functionality to the semiconductor surface,^{1,2} with potential applications in molecular electronics,³ data storage,⁴ and sensing.⁵ In vacuum environments, recent surface science studies have focused on the cycloaddition of linear and cyclic alkenes to the reconstructed Si(100)- 2×1 surface.² For example, cycloaddition of the simplest and smallest alkene, ethylene, has been studied extensively by photoelectron spectroscopy.^{6–12}

The unreconstructed Si(111)- 1×1 surface, which can be made atomically flat on the scale of hundreds of Å through simple solution etching procedures that produce hydrogen termination of the silicon, provides another model substrate for the study of surface modification chemistry.¹³ Recent studies of the ambient pressure modification of Si(111) surfaces have focused on the preparation of straight-chain alkyl overlayers by wet chemical methods such as exposing the hydrogen- or halide-terminated Si surface to alkylmagnesium or alkyllithium reagents,^{14–16} or by the free radical activation of a terminal alkene.^{17–20} Conceptually, the simplest surface/overlayer interface that can be produced is the methyl-terminated Si(111) surface, Si(111)-CH₃. Scanning tunneling microscopy (STM) studies have shown that the CH₃-terminated Si(111) surface is atomically flat and is terminated by close-packed methyl groups.²¹ Photoelectron dif-

fraction studies of the C $1s$ component of silicon-bound carbon atoms on Si(111)-CH₃ have indicated that silicon-carbon bond length is 0.185 nm.¹⁵ Studies of the Si $2p$ core level emission have revealed a 0.27 eV chemical shift for the silicon surface atoms that are bonded to methyl groups.²² An angle-resolved ultraviolet photoelectron spectroscopy study of Si(111)-CH₃ surfaces has been reported.²³ To date, however, there is no information on the detailed valence band electronic structure or on the thermal stability of well-ordered methyl-terminated Si surfaces. The work reported herein describes synchrotron x-ray photoelectron spectroscopy data at high spectral resolution of the chemical and electronic structure of CH₃-terminated Si(111) surfaces that have previously been determined to be both chemically and morphologically ideal.^{14,21}

II. EXPERIMENT

The samples were pieces of n -type silicon(111) wafers which had been doped with Sb to a resistivity of 0.005–0.02 Ω cm. This dopant concentration translates into a Fermi level position, E_F , of $|E_F - E_{v,\text{bulk}}| = 1.04(2)$ eV from the valence band maximum energy, E_v , in the bulk of the silicon samples. Before chemical functionalization, each sample was cleaned by rinsing in H₂O, CH₃OH, acetone, CH₃OH, and H₂O, followed by drying under a stream of N₂(g). Hydrogen-terminated surfaces were prepared by immersion of the cleaned Si samples into 40% NH₄F(aq). This process has been shown to result in a flat (111) surface in which the atop Si atoms are terminated by H atoms.²⁴ Imme-

diately after etching the samples were moved into a $N_2(g)$ -purged glove box for further functionalization. The H-Si(111) surfaces were then chlorinated according to previously published procedures^{14,25} using a saturated solution of PCl_5 in chlorobenzene, to which a few grains of benzoyl peroxide were added to initiate a radical reaction. The solution was heated at 90–100 °C for 45 min, then rinsed thoroughly with tetrahydrofuran (THF) and CH_3OH , and dried under a stream of $N_2(g)$. The Cl-terminated Si(111) surface was then immersed in a 3.0 M solution of CH_3MgCl in THF (Aldrich) and was heated at 70–80 °C for 3 h. Excess THF was added to the reaction vessel to allow for solvent replacement. The sample was then removed from the reaction solution and was rinsed with copious amounts of THF and CH_3OH , then immersed in CH_3OH and removed from the N_2 -purged glove box. The sample was sonicated for 5 min in CH_3OH , sonicated in CH_3CN for a further 5 min, and then dried under a stream of $N_2(g)$. Previous work has shown that this sonication is crucial for complete removal of Mg salts from the methylmagnesium chloride solution.^{14,25} The CH_3 -terminated sample was then sealed under $N_2(g)$, shipped from California to the BESSY II facility in Germany, and put in nitrogen purged glove box. The sample was analyzed approximately 2 weeks after preparation. All results reported herein are from one representative sample, but five samples from two independent preparation runs showed very similar behavior to that reported herein.

Synchrotron x-ray photoelectron spectroscopy (SXPS) experiments were performed at the undulator beamline U49/2-PGM2 of the BESSY II synchrotron facility in Berlin. After introduction into the vacuum system of the SoLiAS experimental station,²⁶ the samples were heated to about 450 °C for 15 min to desorb adventitious nonmethyl hydrocarbons from the surface. The line shapes of the methyl- and silicon-related emissions remained essentially unchanged after annealing. The properties of unannealed surfaces and the changes observed upon annealing will be described elsewhere.²⁷ Photoelectron spectra were recorded with a Phoibos model 150 electron analyzer (SPECS) using photon energies, $h\nu$, between 115 and 650 eV. Spectra of the valence band region were acquired with He I radiation from a UV lamp ($h\nu=21.2$ eV). The overall instrument resolution for the monochromator and analyzer was 80 meV in the Si $2p$ region ($h\nu=150$ eV) and 160 meV in the C $1s$ region ($h\nu=330$ eV). The photoemission energy scale was referenced to the Fermi energy of an evaporated gold film by calibration experiments using $h\nu=150$ eV excitation. To prevent synchrotron beam irradiation damage, the synchrotron beam intensity was reduced such that the photoelectron spectra remained unchanged within the measurement time. The photoelectron emission lines were fitted using symmetric Voigt profiles, after subtraction of a Shirley-type background. The synchrotron-excited spectra were acquired under normal emission, whereas the ultraviolet-excited photoelectron spectra were measured under an emission angle, θ_e , of 28°. The analyzer was operated in an angle-integrating mode with an acceptance angle of a few degrees. Low-energy electron diffraction (LEED) measurements were performed using a three-grid reverse-view LEED system (VG).

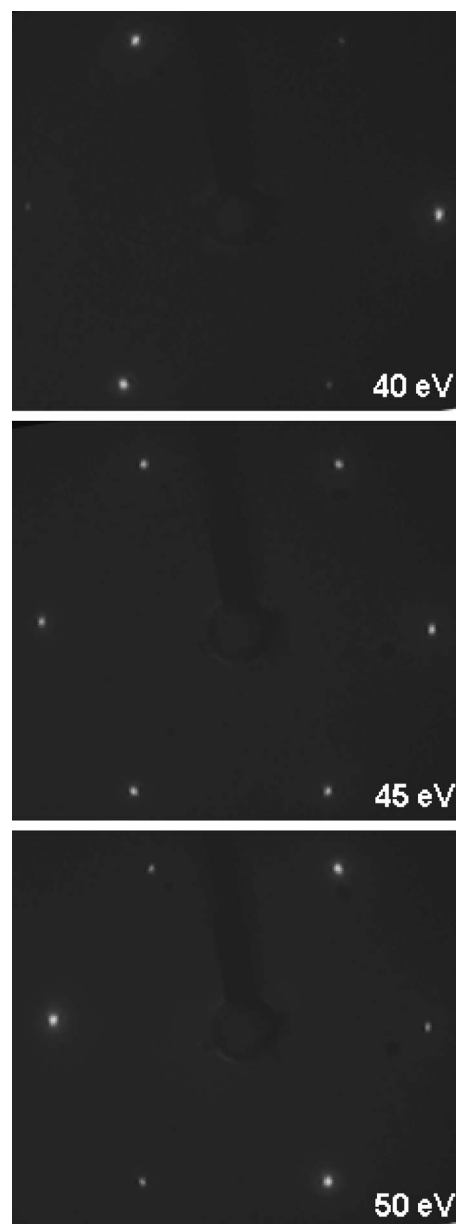


FIG. 1. Low-energy electron diffraction pattern of a Si(111)- CH_3 surface, taken with primary electron energies of 40–50 eV.

III. RESULTS AND DISCUSSION

Figure 1 shows the low-energy electron diffraction patterns of a methyl-terminated Si(111) surface at primary electron energies from 40 to 50 eV. These energies were used because they produced a low electron escape depth. The observed diffraction patterns exhibited a threefold symmetry corresponding to a (1×1) structure. This pattern is consistent with expectations for ideal, close-packed, methyl termination on Si(111). The low intensity of the background, and the sharpness of the diffraction spots, indicate that the surface was well-ordered and consisted of extended, atomically flat terraces with relatively few defects. The low level of diffuse background, even at low electron kinetic energies, indicates that the diffraction pattern is the result of a com-

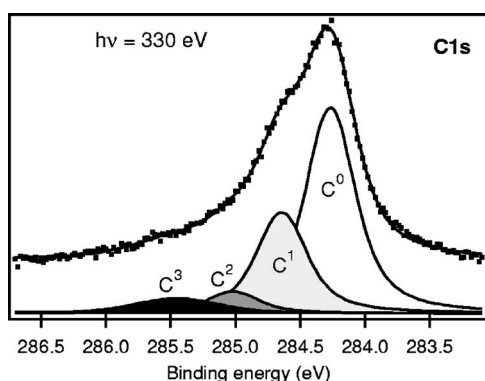


FIG. 2. Carbon 1s emission of Si(111)-CH₃ excited with $h\nu=330$ eV. The asymmetry towards high binding energies is revealed as a vibrational fine structure. Assignment: component C⁰=CH₃-Si (vibrational ground state); C¹, C²=CH₃-Si (C-H stretch vibrations excited, 1st + 2nd excited states); C³=non-CH₃ species. The fitting parameters are given in Table I.

mensurate CH₃ layer on top of a well-ordered Si(111) surface layer. The LEED patterns are fully consistent with recent STM images of such surfaces, which have also shown a (1 × 1) structure at 77 K on such surfaces.^{21,28}

Figure 2 displays the carbon 1s core level emission spectrum of Si(111)-CH₃ excited with $h\nu=330$ eV. The C 1s emission signal exhibited an asymmetry toward the high binding energy side, and displayed a fine structure that consisted of four components, denoted as Cⁿ ($n=0,1,2,3$). The C⁰ signal, at a binding energy of 284.27 eV, represents the adiabatic peak that is assigned to the silicon-bonded carbon atoms of the methyl groups. To deconvolute the C 1s emission data, the binding energy shifts of C¹ and C² were coupled to each other by $\Delta BE_2=2 \times \Delta BE_1$, and ΔBE_1 and the relative intensities were adjusted freely in the fitting process. The resulting fitting parameters and values are given in Table I. The energy shift ΔBE_1 , was found to be 0.38(0.01) eV. The C¹ and C² signals are therefore assigned to satellite peaks that have the same initial state origin as C⁰ but which have vibrational losses of the final state due to the generation of the first and second excited state of C-H stretching vibrations. The final state losses lead to the equidistant shift of C¹ and C² to apparent higher binding energies. Analogous vibrational fine structure in the C 1s photoelectron region has been observed previously in gas phase spectroscopic measurements of methane,²⁹ and has been reported for ethylidyne (C₂H₃) chemisorbed on Rh(111),³⁰ methoxy (CH₃O) on

TABLE I. Fit parameters for the deconvolution of the C 1s emission (Fig. 2) using four components. The Lorentzian width was 0.15 eV for all components.

Component	Binding energy (eV)	(Relative) intensity	Gaussian width (eV)
C ⁰	284.27	1	0.26
C ¹	+0.38	0.49	0.27
C ²	+0.76	0.11	0.28
C ³	+1.2	0.07	0.60

Cu(100),³¹ and for ethylene (C₂H₄) and acetylene (C₂H₂) on Si(001).⁶ The value for $h\nu_{C-H}=0.38(0.01)$ eV deduced for methyl-terminated Si compares well with the excitation energies of 0.385(0.010) eV (Ref. 30) and 0.370(0.020) eV (Ref. 6) reported for other adsorbate systems. The data of Fig. 2 therefore suggest that the asymmetry observed in the C 1s emission of small hydrocarbon adsorbates on silicon^{6,8,10,11} is in fact a multiplex fine structure related to C-H bond vibrational losses.

Component C³ in Fig. 2 is attributed to adventitious aliphatic hydrocarbons that remained on the surface after the annealing step. The C³ peak was present on the nonannealed surface, and annealing reduced the relative area of C³ by a factor of 4, but the line shape of the methyl- and silicon-related emissions remained essentially unchanged (not shown).²⁷ The relative intensity of component C³ in Fig. 2, was 7% of the total carbon observed. The 1.2 eV chemical shift of the adventitious hydrocarbon with respect to the energy of silicon-bonded CH₃ groups compares well to the value of 1.1 eV observed on Si(111)-CH₃ by Terry *et al.*²² although the relative intensity of the methyl-related signal was much smaller in that study than on the samples studied herein.

Figure 3(a) displays the photoelectron spectra of the Si 2p core level recorded with excitation energies between $h\nu=150$ eV and $h\nu=650$ eV. For ideal methyl-termination of the surface, a bulk Si signal and a single surface component arising from surface silicon atoms bonded to the methyl group are expected. Indeed, two components of the signal, denoted S and B, of approximately equal intensity, were clearly observed for $h\nu=150$ eV, which produces an inelastic electron mean free path, λ , of ≈ 0.4 nm (Refs. 32, 33) and thus high surface sensitivity. The intensity of component S decreased significantly for higher excitation energies, indicating that S arises from the surface Si atoms.

The silicon 2p emission was deconvoluted into a surface component S and bulk component B [Fig. 3(b)], and the corresponding fit parameters for the $h\nu=150$ eV spectrum are given in Table II. The chemical shift of the methyl-bonded silicon atoms was 0.30(0.01) eV. This value is somewhat higher than that observed on surfaces prepared using a slightly different, more reactive chlorination method,²² but is in accord with independent measurements on methylated surfaces recorded recently.³⁴ The chemical shift of the Si atoms bound to C clearly indicates that the Si is positively charged in its bond polarity, as expected based on the relative electronegativities of C and Si (2.55 and 1.90, respectively).³⁵

A quantitative relation of the core level intensities to the density of surface species was complicated by the presence of photoelectron diffraction effects. In fact, when varying the excitation energy from 115 to 200 eV, an oscillating deviation of the measured surface component intensity was observed relative to the intensity ratio expected³³ from the corresponding escape depth. A detailed account of this phenomenon on our Si(111)-CH₃ surfaces will be given elsewhere.²⁷

The high surface quality of the wet-chemically prepared Si(111)-CH₃ samples is underscored by the low residual surface oxide concentrations observed. This is illustrated by Fig.

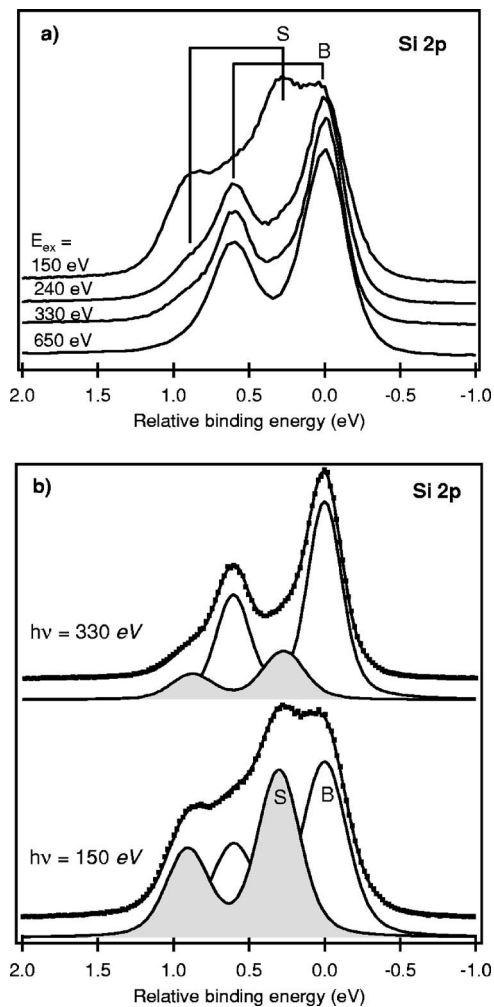


FIG. 3. Si 2p core level spectra of Si(111)-CH₃ taken with varying excitation energies. The highest surface sensitivity is obtained for $h\nu=150$ eV. The Si 2p emission is composed of a bulk component (B) and a surface component (S) which is shifted to higher binding energies by $0.30(\pm 0.01)$ eV. Fitting results are shown in (b), and the corresponding fit parameters are given in Table II.

4, where the same Si 2p emission as in Fig. 3 ($h\nu=150$ eV) is enlarged and displayed in a broader energy range including the SiO₂ spectral range. The weak emissions around a binding energy of 103 eV are due to silicon dioxide, Si⁺⁴ and Si⁺³ suboxide. To quantify the Si⁺¹ suboxide component, in addition to the bulk- and methyl-related components B and S, silicon oxide peaks (Si⁺¹, Si⁺³, Si⁺⁴) with

TABLE II. Fit parameters for the deconvolution of the Si 2p emission, plotted in Fig. 3. The Lorentzian width for both components was 0.055 eV. The spin-orbit splitting was fixed at 0.605 eV and the branching ratio was set to 0.52 (Ref. 48).

Component	Binding energy (eV)	(Relative) intensity	Gaussian width (eV)
Bulk B	99.68	1	0.29
Surface S	+0.30	0.96	0.27

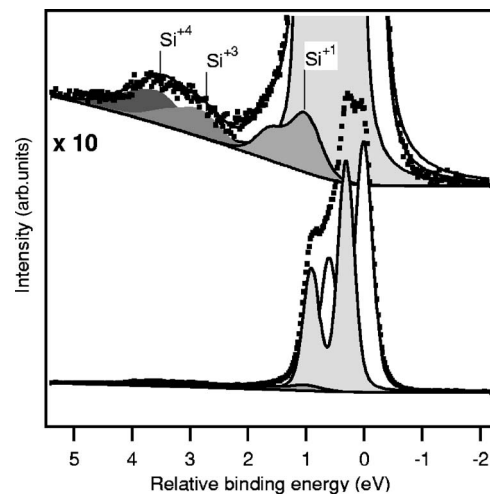


FIG. 4. Curve fitting to the Si 2p emission in Fig. 3 ($h\nu=150$ eV) including weak (sub)oxide Si⁺¹, Si⁺³, and Si⁺⁴ components, which have been magnified by a factor of 10 for better visibility. The intensity of the Si⁺¹ component depends on the assumed background (here: Tougaard-type) but is always less than 5% of the Si-CH₃ component.

chemical shifts of +3.5, +2.7, and +1.0 eV (Ref. 36) were included in the fit to the data of the entire Si 2p energy range. The resulting intensity of the Si⁺¹ component relative to the bulk Si⁰ emission depended on the shape of the background, and varied between 1% for a Shirley-type background [Fig. 3(b)], and 4% for a Tougaard-type background, as displayed in Fig. 4. Considering the wet chemical *ex situ* preparation of the samples and their transport under N₂(g) from California to Berlin between preparation and analysis, the surface quality is remarkable and underscores the chemical stability of the Si(111)-CH₃ surface.

Figure 5 displays spectra of the valence band region recorded with $h\nu=150$ and 21.2 eV (He I radiation). The methyl-terminated Si(111) surface showed valence band emissions at 16.6, 9.8 (He I), 7.7, 5.44 eV, a shoulder at 4.8 eV (He I), and from 2 to 4 eV. The He I-excited spectrum was measured under an emission angle, ϑ_e , of 28°, where the sharp emission signal at 5.44 eV is prominent. A detailed angular study was not performed, but the behavior reported by Miyadera *et al.*,²³ in which the 5.4 eV feature is not observed in normal emission, but is prominent and sharp for emission angles $>24^\circ$, was observed in our studies as well.

The main spectral features have been observed previously for Si(111)-CH₃ surfaces prepared by a slightly different method,²³ but the spectral features appear more pronounced in the present data, consistent with the high quality of the surface termination layer also indicated by the electron diffraction data for surfaces prepared using the two-step chlorination/alkylation procedure. By comparison with the gas phase spectra of methane³⁷ and cluster calculations,²³ the emission at 16.6 eV can be attributed to the C 2s orbitals, and the peaks at 7.7 and 5.4 eV are assigned to C 2p-derived orbitals. The emission feature near 7.7 eV is assigned to the C-H bonds of the methyl groups. Methyl-related emissions have been reported previously at 8.5 and 8 eV in the ultraviolet photoelectron spectra of methyl iodide adsorbed on Pd

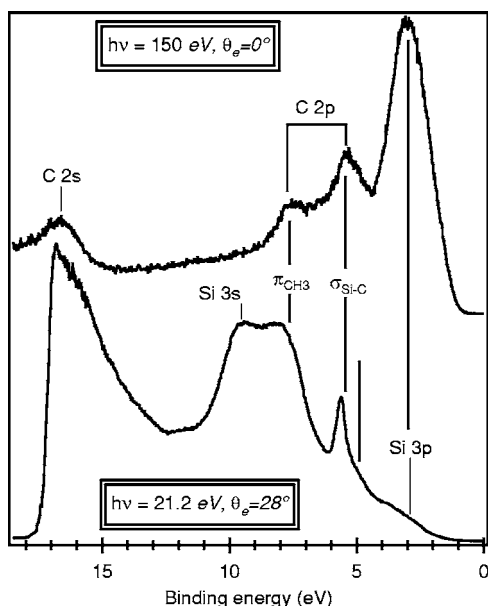


FIG. 5. Valence band spectra of Si(111)-CH₃ excited with He I radiation $h\nu=21.2$ eV (bottom) or with synchrotron radiation with $h\nu=150$ eV (top). The spectra were acquired under the emission angles θ_e given in the figure. Through comparison to the cluster calculations (Ref. 23) and gas phase spectra (Ref. 37), the emission structures have been assigned as indicated.

(100) (Ref. 38) or methyl silane on Cu(111), respectively.³⁹ Since adsorption of methyl groups on the surface Si(111) atoms corresponds to an adsorption geometry having C_{3v} symmetry, the molecular orbitals of the methyl group have e symmetry with (pseudo-) π_{CH_3} character.

The emission at 5.44 eV is assigned to the σ_{Si-C} bonds between the substrate and the methyl overlayer. Recent MO calculations on H_3CSiH_3 have shown that the σ_{Si-C} bond with a_1 symmetry is situated about 2.5 eV above the π_{CH_3} orbitals.³⁹ Additionally, comparison to the gas phase spectra of methyl silanes $Si_n(CH_3)_{2n+2}$ ($n=1,2,3,4$),⁴⁰ and assuming an extra molecular polarization relaxation of ~ 2 eV, supports the assignment of the 7.7 and 5.4 eV structures to the π_{CH_3} and σ_{Si-C} bonds, respectively. The assignment of the 5.4 eV structure to a surface state is also evident from the non-dispersive behavior observed previously.²³

The Si-C bond related emissions of Si(111)-CH₃ should be similar to the emissions of the well-known hydrogen-terminated Si(111)-H surface. The sigma-bonding between the silicon dangling bond (sp^3 hybrid) and the orbital of the adsorbate, be it hydrogen or the methyl group, leads to a similar bonding configuration and corresponding bond orbital energy structure. For Si(111)-H, three surface-state related emissions are observed at 8.6, 4.8, and 3.8 eV.⁴¹ In the Si(111)-CH₃ spectrum, including the prominent emission at 5.4 eV, corresponding structures can be identified at 9.8, 5.4, and 4.8 eV. The emission at 9.8 eV resides in the region of the Si 3s-derived valence bands, thus this emission is evidently a surface resonance.⁴² The assignment of the shoulder at 4.8 eV as being part of the Si-C-related emissions is tentative and needs to be corroborated by additional angle-resolved studies.

The degree of surface band bending provides a measure of the quality of the electronic passivation of a semiconductor surface. In the ideal case for a surface without band bending, when all surface states are chemically passivated and electronically inactive, the so-called flat-band condition should be produced. The degree of surface band bending can be derived from a comparison between the positions of the Fermi level at the surface vs. the bulk. The surface Fermi level position of Si(111)-CH₃ was derived from the binding energy of the Si 2p bulk component relative to the Fermi energy, which is 99.68 eV (cf. Table II). The binding energy of the Si 2p signal with respect to the valence band maximum (VBM, E_v) is known to be 98.74(4) eV,⁴³ which implies a difference of 0.94 eV from the VBM to the Fermi energy, E_F , at the surface $|E_F - E_v|$. The bulk Fermi level is expected to be at $|E_F - E_v|_{bulk} = 1.04(2)$ eV, as derived from the bulk conductivity of the Si samples used in our work. Taking the Si 2p binding energy from the literature, and estimating the error in the surface band bending to ± 0.1 eV yields a value of 0.10 ± 0.10 eV between the surface and bulk Fermi level positions. Hence, the surface is close to the flat-band condition, with a surface band bending smaller than 0.2 eV.

From extrapolation of the secondary electron cutoff, the work function, $W_F = E_{vac} - E_F$, of the methyl-terminated surface was found to be 3.86 eV. From this value, the electron affinity, χ , of the methyl-terminated Si(111) surface was calculated according to

$$\chi = E_{vac} - E_c = E_{vac} - E_F + E_F - E_c = W_F - (E_g - |E_v - E_F|).$$

With $E_g = 1.12$ eV and the measured values given above, an electron affinity of 3.68 eV was obtained for Si(111)-CH₃ surfaces. This value may be compared to other Si surface terminations as $\chi[Si(111):H] = 4.17$ eV,^{44,45} $\chi[Si(111)-(7 \times 7)] = 4.16$ eV,³⁶ and $\chi[Si(100)-(2 \times 1)] = 4.21$ eV.³⁶ Estimating the electron affinity of bulk silicon as 4.05 eV,⁴⁶ the surface dipole δ caused by the methyl monolayer was calculated to be ~ -0.4 eV.

Figure 6 summarizes the surface potentials of the Si(111)-CH₃ surface to give the surface band diagram. Geometrically, the methyl-terminated Si surface is comprised of a series of atomic layers, with a composition -Si-CH₃. The electric dipole of this surface was determined by the bond charge distribution between these layers, which was estimated from the Pauling electronegativities of 1.90, 2.55, and 2.20 for Si, C, and H, respectively.³⁵ The observed lowering of the electron affinity by methyl-termination indicates that the electric dipole moment of the oriented methyl groups, with charge distribution $C^\delta - H_3^\delta$, dominates the electric dipole moment of the surface. The effective decrease of the silicon electron affinity by the methyl adsorbate is complementary to silicon surface engineering by grafting of benzene derivatives, in which the dipole moment of nitro- or bromobenzene adsorbates effectively increases the electron affinity of the silicon sample.⁴⁷

IV. SUMMARY AND CONCLUSIONS

The photoelectron spectra of methyl-terminated Si(111) surfaces prepared in a wet-chemical two-step chlorination/

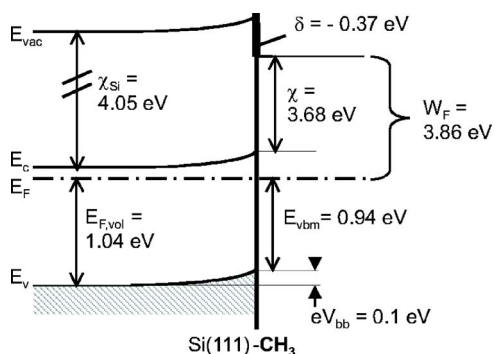


FIG. 6. Surface energy band diagram of the Si(111)-CH₃ surface. The surface is close to flat band conditions with a residual surface band banding, eV_{bb} , of 0.1 eV. The electron affinity, χ , of Si(111)-CH₃ is ≈ 3.7 eV, which indicates a surface dipole, δ , of -0.4 eV. The position of the valence band maximum at the surface, $|E_F - E_v| = 0.94$ eV, is inferred from the Si $2p_{3/2}$ binding energy, where a core level-to-valence band separation $BE_v(\text{Si } 2p_{3/2})$ of 98.74 eV was assumed (Ref. 43).

alkylation technique have been analyzed in detail. A vibrational fine structure in the single-component carbon 1s emission was clearly resolved. The excitation of C-H stretching vibrations with $h\nu_{\text{C-H}} = 0.38 \pm 0.01$ eV caused corresponding loss features on the high binding energy side of the C 1s emission. The methyl-bonded silicon surface atoms exhibited

a chemical shift of the Si $2p$ emission of 0.30 ± 0.01 eV. In the valence band region, characteristic emissions at 5.44 and 7.7 eV arose from the Si-C $\sigma_{\text{Si-C}}$ bonds and the π_{CH_3} molecular orbitals of the methyl group, respectively. The sharp $\sigma_{\text{Si-C}}$ emission may act as a fingerprint for this well-ordered surface. Electronically, the methyl-terminated Si(111)-CH₃ surface was close to the flat-band condition and exhibited a surface dipole of ~ -0.4 eV. The methyl-terminated Si(111) surfaces were chemically and thermally stable, withstanding a vacuum anneal at 450 °C. Even when such an anneal was performed after 2 weeks of storage under N₂(g) between preparation and analysis, the surface silicon oxide coverage was below 5% of a monolayer. Nearly ideal passivation of Si(111) surfaces can therefore be achieved by methyl termination with the two-step chlorination/alkylation process.

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