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What a Difference a Bond Makes: The Structural, Chemical, and Physical Properties of Methyl-Terminated Si(111) Surfaces

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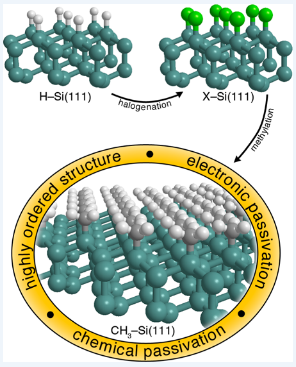

CONSPECTUS: The chemical, electronic, and structural properties of surfaces are affected by the chemical termination of the surface. Two-step halogenation/alkylation of silicon provides a scalable, wet-chemical method for grafting molecules onto the silicon surface. Unlike other commonly studied wet-chemical methods of surface modification, such as self-assembly of monolayers on metals or hydrosilylation on silicon, the two-step method enables attachment of small alkyl chains, even methyl groups, to a silicon surface with high surface coverage and homogeneity. The methyl-terminated Si(111) surface, by comparison to hydrogen-terminated Si(111), offers a unique opportunity to study the effects of the first surface bond connecting the overlayer to the surface. This Account describes studies of methyl-terminated Si(111), which have shown that the H−Si(111) and CH_3−Si(111) surfaces are structurally nearly identical, yet impart significantly different chemical and electronic properties to the resulting Si surface.

The structure of methyl-terminated Si(111) formed by a two-step halogenation/methylation process has been studied by a variety of spectroscopic methods. A covalent Si−C bond is oriented normal to the surface, with the methyl group situated directly atop a surface Si atom. Multiple spectroscopic methods have shown that methyl groups achieve essentially complete coverage of the surface atoms while maintaining the atomically flat, terraced structure of the original H−Si(111) surface. Thus, the H−Si(111) and CH_3−Si(111) surface share essentially identical structures aside from the replacement of a Si−H bond with a Si−C bond.

Despite their structural similarity, hydrogen and methyl termination exhibit markedly different chemical passivation. Specifically, CH_3−Si(111) exhibits significantly greater oxidation resistance than H−Si(111) in air and in aqueous electrolyte under photoanodic current flow. Both surfaces exhibit similar thermal stability in vacuum, and the Si−H and Si−C bond strengths are expected to be very similar, so the results suggest that methyl termination presents a greater kinetic barrier to oxidation of the underlying Si surface. Hydrogen termination of Si(111) provides nearly perfect electronic passivation of surface states (i.e., less than 1 electronic defect per 40 million surface atoms), but this electronic passivation is rapidly degraded by oxidation in air or under electrochemical conditions. In contrast, methyl termination provides excellent electronic passivation that resists degradation due to oxidation. Moreover, alkylation modifies the surface electronic structure by creating a surface dipole that effectively changes the electron affinity of the Si surface, facilitating modification of the charge-transfer kinetics across Si/metal or Si/electrolyte junctions.

This Account also briefly describes recent studies of mixed monolayers formed by the halogenation/alkylation of silicon. Mixed monolayers allow attachment of bulkier groups that enable secondary chemistry at the surface (e.g., attachment of molecular catalysts or seeding of atomic layer deposition) to be combined with methyl termination of remaining unreacted surface sites. Thus, secondary chemistry can be enabled while maintaining the chemical and electronic passivation provided by complete termination of surface atoms with Si−C bonds. Such studies of mixed monolayers demonstrate the potential use of a wet-chemical surface modification scheme that combines both chemical and electronic passivation.

I. INTRODUCTION

The chemical termination of the surfaces of solids is well-known to dramatically influence the electronic, chemical, and structural properties of the resulting materials. The chemistry of semiconductor or metal surfaces has classically been probed by dosing and annealing well-defined surfaces under carefully controlled conditions in ultrahigh vacuum. Wet chemical, scalable methods of surface functionalization have generally exploited self-assembled monolayers on metals such as Au, Cu, and Ag.[1,2] For such systems, a direct elucidation of the effects of changing the first surface bond is difficult; the use of short alkyl chains in surface ligation, to allow for direct spectroscopic probing of the surface bonding and structure, generally yields disordered overlayers that are incompletely terminated and/or structurally ill-defined.

A prominent exception is the termination of the Si(111) surface by H atoms. Etching Si(111) surfaces in $NH_4F(aq)$ produces large, atomically flat terraces, in which each Si atop site has three tetrahedral sp^3 hybridized orbitals projecting down into the solid, with the fourth sp^3 hybrid orbital oriented normal to the surface plane, allowing for termination of every Si atop site with a covalent Si−H bond normal to the (111) surface plane. Due to their well-defined structure and thermal

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stability in vacuum, H−Si(111) surfaces have been widely investigated by a number of spectroscopic methods and also have been used in a variety of surface physics experiments to characterize the properties of this extremely interesting chemically functionalized semiconductor surface.[3−6]

The Si−H bonds on H−Si(111) surfaces are however unstable toward oxidation in air and toward anodic electrochemical processes in solution. Simple theoretical considerations moreover indicate that the surface electronic structure, surface reactivity, and the surface-state energies should be very sensitive to the nature of the bonding of the atop Si sites on the Si(111) surface. The Si−H and Si−C bond energetics are similar so functionalization of the surface with Si−C termination is clearly of interest. The only straight chain saturated alkyl group that sterically can terminate every atop site on an unreconstructed Si(111) surface is a methyl group, because the distance between Si atop sites is 3.8 Å, as compared to the 2.2 Å van der Waals radius of a methyl group. Fortunately, wet chemical methods have been developed that allow the preparation of remarkably chemically and structurally well-defined CH_3−Si(111) surfaces. This Account reviews the preparation, characterization, and properties of these CH_3−Si(111) surfaces, and compares their chemical and physical behavior to that of H−Si(111) surfaces, to directly reveal the difference that one surface termination bond (H−Si vs C−Si) makes in the properties of these well-defined, interesting, and important semiconductor surfaces.[3−12]

Although Si(111) has been extensively functionalized using hydrosilylation,[4,5,8−10] this method is inherently unable to produce methyl-terminated Si and thus to allow for termination of every Si atop site in a defined fashion.[13,14] Methylation of the Si(111) surface has, however, been demonstrated using a two-step halogenation/alkylation scheme (Figure 1).[15] In the first step, a H−Si(111) substrate (produced by NH_4F etching) is halogenated in a saturated chlorobenzene solution of PCl_5 containing a radical initiator, to produce a Cl−Si(111) surface. Other methods of halogenation have also been used to obtain nominally the same X−Si(111) surface (X = Cl, Br, I).[8] In the second step, the X−Si(111) surface is reacted with an organolithium or Grignard reagent (most commonly CH_3MgCl), to produce the CH_3−Si(111) surface. Methylation has also been achieved by anodic grafting to, or Grignard reaction with, H−Si(111),[16−21] but the two-step method remains more common and to date yields more chemically, structurally, and spectroscopically defined surfaces.

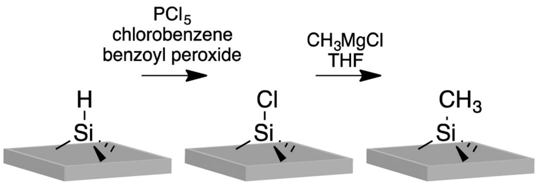

Figure 1. Schematic of a common two-step chlorination and methylation procedure for the Si(111) surface.

II. STRUCTURAL CHARACTERIZATION

A variety of detailed spectroscopic studies have indicated that CH_3−Si(111) surfaces indeed consist of methyl groups that are bonded on essentially every Si atop site and that are oriented normal to the Si(111) surface plane. Specifically, high resolution electron energy loss spectroscopy (HREELS) of CH_3−Si(111) revealed a Si−C stretching peak at 678 cm^{-1}, indicating covalent bonding of methyl groups to the Si surface.[17,22,23] Fourier-transform infrared (FTIR) spectroscopic studies of the CH_3−Si(111) surface then confirmed the presence of a Si−C stretching mode, polarized normal to the surface, at 678 cm^{-1}.[24,25] Transmission FTIR spectra of a CH_3−Si(111) surface collected with the incident IR beam oriented at 30° or 74° relative to the surface normal exhibited a sharp peak attributed to Si−C stretching at 74° incidence but showed essentially no signal at 30° incidence (Figure 2). The light incident at 74° excites modes polarized both parallel and perpendicular to the surface, whereas the light incident at 30° primarily excites modes polarized parallel to the surface. A similar angular dependence was observed for the methyl umbrella mode at 1257 cm^{-1}, and the IR data collectively indicate that the methyl group is oriented normal to the surface, as expected for methyl groups bonded atop the surface Si atoms. Furthermore, the angular dependence suggests that the surface is not roughened significantly upon methylation, as atomic level roughness would lead to some methyl groups attached with the Si−C bond not normal to the surface and, thus, Si−C stretching and methyl umbrella absorption in the spectra collected with light at 30° incidence.

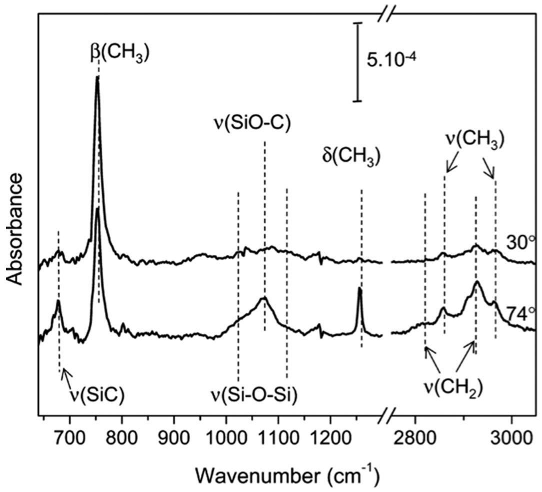

Figure 2. Transmission FTIR spectra of a CH_3−Si(111) surface collected with the unpolarized IR beam incident at 30° and 74°, respectively, relative to the surface normal. Both spectra are referenced to the Cl−Si(111) surface. Reprinted with permission from ref 24. Copyright 2007 American Chemical Society.

Additional evidence for the formation of a covalent Si−C bond has been obtained using soft X-ray photoelectron spectroscopy (SXPS), which probes the CH_3−Si(111) surface with high surface sensitivity and resolution.[26−29] Figure 3 shows the Si 2p core-level spectra of a CH_3−Si(111) surface collected using two different excitation energies. The spectra display the distinct signals from the bulk Si (B) and the surface Si (S). The surface sensitivity was maximized for $h\nu$ = 150 eV (inelastic electron mean free path ~0.4 nm), and component S decreased with increasing excitation energies, consistent with component S arising from surface Si atoms. Moreover, component S was shifted 0.30 eV higher in binding energy relative to component B, indicating a positive charge on the surface Si atoms, consistent with the expectation for Si covalently bonded to C based on the higher Pauling electronegativity of C (2.55) than Si (1.90).

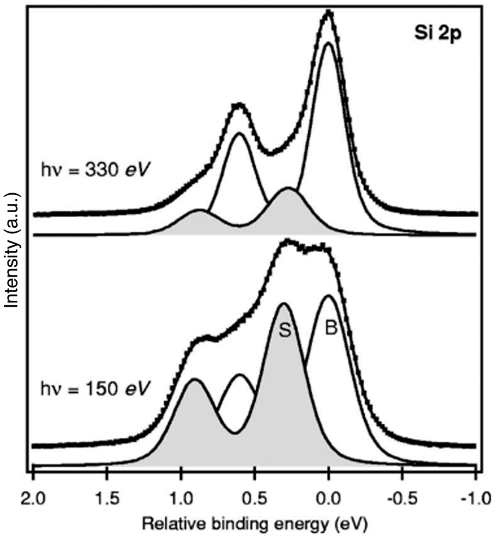

Figure 3. High-resolution Si 2p core-level spectra of CH_3−Si(111) collected with 330 eV (top) and 150 eV (bottom) excitation energies shown with curve fits. Maximum surface sensitivity was obtained with $h\nu$ = 150 eV. Spin−orbit doublets corresponding to the bulk Si (B) and surface Si (S, shifted 0.30 eV higher in binding energy) are fit to the experimental data. Adapted with permission from ref 26. Copyright 2005 by the American Physical Society.

By showing a peak at ∼284 eV binding energy, the C 1s core-level SXPS data complemented the SXPS Si 2p spectra in demonstrating the formation of a covalent Si−C bond on the methylated Si(111) surface.[26,29−34] Aliphatic carbon bonded only to carbon and hydrogen typically yields a C 1s peak centered at ∼285 eV; therefore, a C 1s peak observed near 284 eV is shifted ∼1 eV lower in binding energy relative to aliphatic carbon, corresponding to an increased electron density on C, and consistent with a covalent Si−C bond according to the relative electronegativities of Si and C.

Photoelectron diffraction (PED) data from fitted C 1s spectra collected using varying photon energies have been used to measure the Si−C bond length in methyl- and pentyl-terminated Si(111) prepared by halogenation/alkylation and hydrosilylation, respectively.[34] Several models were fit to the PED data, and in both cases a Si−C bond length of 1.85 Å with the carbon bonded directly atop a surface silicon atom yielded the best fit. The Si−C bond length of 1.85 Å is similar to that of the covalent Si−C bonds in alkylsilanes,[35] providing further evidence that methylation of Si(111) by halogenation/alkylation does, in fact, form a covalent Si−C bond.

For carefully prepared CH_3−Si(111) surfaces that have not been exposed to air, the Si 2p XPS data exhibit little or no signal due to silicon dioxide or suboxides.[26,27,31,36] Similarly, FTIR spectra exhibit only small absorbances due to Si−O−Si phonon modes or SiO−C bonds, with the oxide coverage estimated to be ∼1.2% of the surface under such conditions.[24] XP survey spectra of properly cleaned alkylated surfaces also have shown no evidence for contamination of the surface by residual halogen or magnesium (lithium) salts from the Grignard (organolithium) precursor.[15,27]

Arguably the most defining feature of the CH_3−Si(111) surface structure is the high surface coverage of terminal methyl groups. The van der Waals radius of a methyl group (∼2.2 Å) is slightly more than half the interatomic spacing of Si atop sites on the Si(111) surface (∼3.8 Å), which in principle allows every Si surface atom to bond to a methyl group (allowing for the fact that methyl groups are not truly spherical).[16] In contrast, the methylene groups of longer alkyl chains have a larger van der Waals radius (∼2.5 Å) that is expected to lead to greater steric strain at high coverages.[27] High-resolution Si 2p SXPS data of CH_3−Si(111) surfaces have indicated a surface coverage of 0.85 monolayers (ML; 1 ML = 1 methyl per surface Si atom),[27] while Si(111) surfaces functionalized with ethyl and other larger hydrocarbons have been shown to have lower surface coverages.[28,31,33,37] Strikingly, low-temperature scanning tunneling microscopy (STM) images of CH_3−Si(111) surfaces have shown very few defects on the surface and have revealed a high degree of order (Figure 4).[38,39] At 77 K, bright triangular protrusions were observed with a spacing of 3.8 Å, identical to the interatomic spacing of Si(111) surface atoms. At 4.7 K, the triangular protrusions were resolved into three smaller spots, separated by an average distance of 1.8 Å, consistent with the separation expected for hydrogen atoms in sp^3-hybridized methyl groups. The STM results showed ∼100% coverage of the Si(111) surface by methyl groups and showed that the surface was not roughened by methylation. Although STM is limited to probing very small areas on the surface, the surface coverage determined by STM (1.0 ML) is in good agreement with the macroscopic (probed area on the order of square millimeters) coverage determined by the Si 2p SXPS (0.85 ML) signal, considering that coverages from XPS analysis are sensitive to the fitting method as well as to various parameters in the substrate-overlayer model. Near 100% termination of surface atoms with methyl groups on a macroscopic scale is also indirectly supported by the chemical and electronic passivation, as discussed below. Polarization-selected sum frequency generation (SFG) of the symmetric and asymmetric C−H stretch modes of CH_3−Si(111) at room temperature have displayed a pronounced azimuthal anisotropy.[40] The observed 3-fold symmetry in registry with the 3-fold symmetry of the Si(111) substrate showed that the methyl groups primarily were in three equivalent energetic minima and jumped between the minima by 120° rotations about the Si−C bond. The SFG

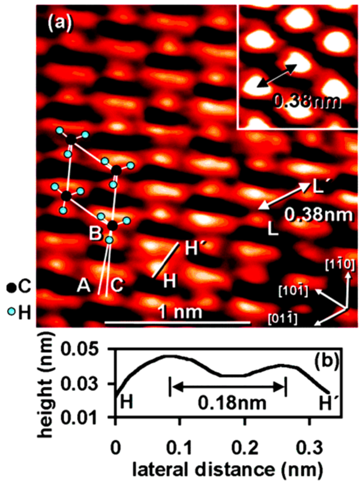

Figure 4. STM image of CH_3−Si(111) collected at 4.7 K (inset: 77 K) with a sample bias of −2.5 V and a constant current of 0.050 nA (dark = low; light = high). Directions of low-index planes determined by X-ray crystallography are shown. The surface unit cell is represented by the parallelogram, and four methyl groups are drawn. Adapted with permission from ref 39. Copyright 2005 American Chemical Society.

data indicated that this rotation occurs on a time scale of 1−2 ps, an order of magnitude slower than the 100 fs rotational dephasing of a free, gas-phase methyl group at room temperature.

Further evidence for the preservation of the surface structure and long-range surface ordering has been obtained by the low-energy electron diffraction (LEED) patterns of CH_3−Si(111), which exhibit a (1 × 1) structure with 3-fold symmetry and sharp, bright spots on a low intensity background.[26,32] Similarly, He diffraction experiments have yielded a lattice constant of 3.82 Å and have exhibited sharp diffraction patterns with minimal diffuse background.[41] Helium atom scattering experiments have been used to probe the Rayleigh wave dispersion relation of CH_3−Si(111) and CD_3−Si(111) surfaces.[42] The Rayleigh wave energy and line shape of CH_3−Si(111) differ from H−Si(111), and density functional perturbation theory calculations indicate that this difference arises from hybridization of the vibrations of the substrate with librations of the overlayer, demonstrating a new aspect of vibrational dynamics at semiconductor−organic interfaces.

III. CHEMICAL PASSIVATION AND STABILITY

Although the Si−H and Si−C bond strengths are very similar, the two different types of surface termination might present different kinetic barriers toward oxidation of the Si surface. Accordingly, the resistance to oxidation in air imparted by different alkylation methods and by hydrogen and chlorine termination has been studied in detail.[36] As shown in Figure 5, H−Si(111) and Cl−Si(111) exhibited similar rates of oxidation in ambient laboratory air, whereas CH_3−Si(111) exhibited negligible oxidation for nearly 50 h and exhibited a significantly reduced rate of oxidation thereafter. These CH_3−Si(111) surfaces, prepared using PCl_5/CH_3MgCl or $Cl_2(g)/CH_3MgBr$, displayed approximately 0.8 and 0.6 equiv monolayers of SiO_2 after 216 and 288 h of air exposure, respectively. For comparison, H−Si(111) displayed a measurable oxidized Si 2p peak after only 4 h of air exposure and displayed 1.4 equiv monolayers of SiO_2 after 216 h. These results, as well as subsequent studies,[24,28,31] have therefore demonstrated the impressive resistance to oxidation that is characteristic of CH_3−Si(111). The mechanism of oxidation of CH_3−Si(111) has not been well-elucidated either experimentally or theoretically to date.

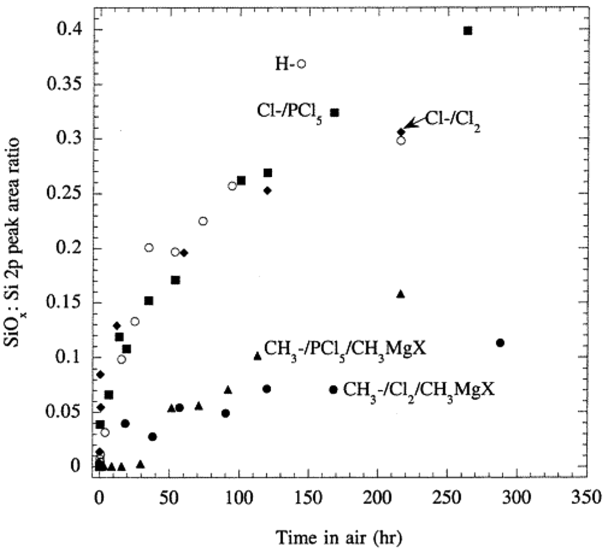

Figure 5. Ratio of the Si 2p peak area due to oxidized Si to the bulk Si 2p peak area for Si(111) surfaces exposed to air for various times: open circles, H−Si(111) prepared by NH_4F etch; squares, Cl−Si(111) prepared using PCl_5; diamonds, Cl−Si(111) prepared using $Cl_2(g)$; triangles, CH_3−Si(111) prepared using PCl_5/CH_3MgCl; closed circles, CH_3−Si(111) prepared using $Cl_2(g)/CH_3MgBr$. Reprinted with permission from ref 36. Copyright 2003 American Chemical Society.

The thermal stability of CH_3−Si(111) surfaces has been studied by XPS analysis after annealing of the surface in ultrahigh vacuum (UHV).[32] CH_3−Si(111) is stable to ≥440 °C, only slightly lower than the thermal stability limit of flat H−Si(111) (∼480 °C).[43] XP spectra obtained after annealing CH_3−Si(111) to 530 °C were consistent with formation of SiC.

The stability of CH_3−Si(111) has also been evaluated under conditions relevant to photoelectrochemical applications.[44−47] Exposure of H−Si(111)/H_2O interfaces to anodic current flow leads to rapid oxidation of the Si surface. In contrast, CH_3−Si(111) photoanodes operated in aqueous electrolyte (0.35 M $K_4Fe(CN)_6$/0.05 M $K_3Fe(CN)_6$) have exhibited much greater stability, sustaining 1 mA cm^{-2} of photoanodic current density for 60 min with little degradation of performance.[45] The top plots in Figure 6 show the Si 2p XP spectra for H−Si(111) and CH_3−Si(111) before and after immersion in $Fe(CN)_6^{3-/4-}(aq)$ electrolyte. H−Si(111) surfaces showed markedly more oxidation (approximately 3 ML of oxide) after immersion than did CH_3−Si(111) surfaces. The bottom plots in Figure 6 show the current density (J) versus potential (E) scans of H−Si(111) and CH_3−Si(111) electrodes. The H−Si(111) surface exhibited initially low open-circuit voltages (V_{oc}) and fill factors, with further deterioration on subsequent scans. In contrast, the CH_3−Si(111) surface showed good rectification and a high fill factor initially, and was much more stable with subsequent scans than the hydrogen-terminated surface.

IV. ELECTRONIC PROPERTIES

H−Si(111) provides excellent electronic passivation of Si surfaces states, and accordingly, measurements of H−Si(111) in contact with HF(aq) have shown a surface recombination velocity (S) as low as 0.25 cm s^{-1}, which corresponds to less than 1 electronic defect per 40 million surface atoms.[48] However, oxidation of the H−Si(111) surface in air or under electrochemical conditions quickly leads to an increase in the number of electronic defects.

In contrast, CH_3−Si(111) surfaces exhibit significantly more stable carrier lifetimes and S values, in accord with the oxidation resistance provided by methyl termination. Figure 7 shows that the charge-carrier lifetimes for CH_3−Si(111) samples stored in air were stable for nearly 30 days.[49] The observed charge-carrier lifetimes (∼300 μs) corresponded to $S \sim 20$ cm s^{-1}, which is equivalent to 1 electronic defect per ∼250 000 surface atoms. H−Si(111) in contact with $H_2SO_4(aq)$ exhibited a longer charge-carrier lifetime (800 μs under high-level injection), but the carrier lifetime was rapidly reduced upon subsequent exposure to air, with lifetimes of ∼10 μs observed within 2 h. In contrast, S values for alkylated Si(111) surfaces have been shown to remain low despite detectable oxidation after exposure to air for days,[31] possibly because Si suboxides—primarily Si^+ and Si^{3+}—formed on alkylated surfaces, whereas SiO_2 formed upon oxidation of H−Si(111) in air. Suboxides appear to be less detrimental to carrier lifetimes than an interfacial layer of native SiO_2.[28] Scanning tunneling spectroscopic studies have shown a very low density of states in the Si

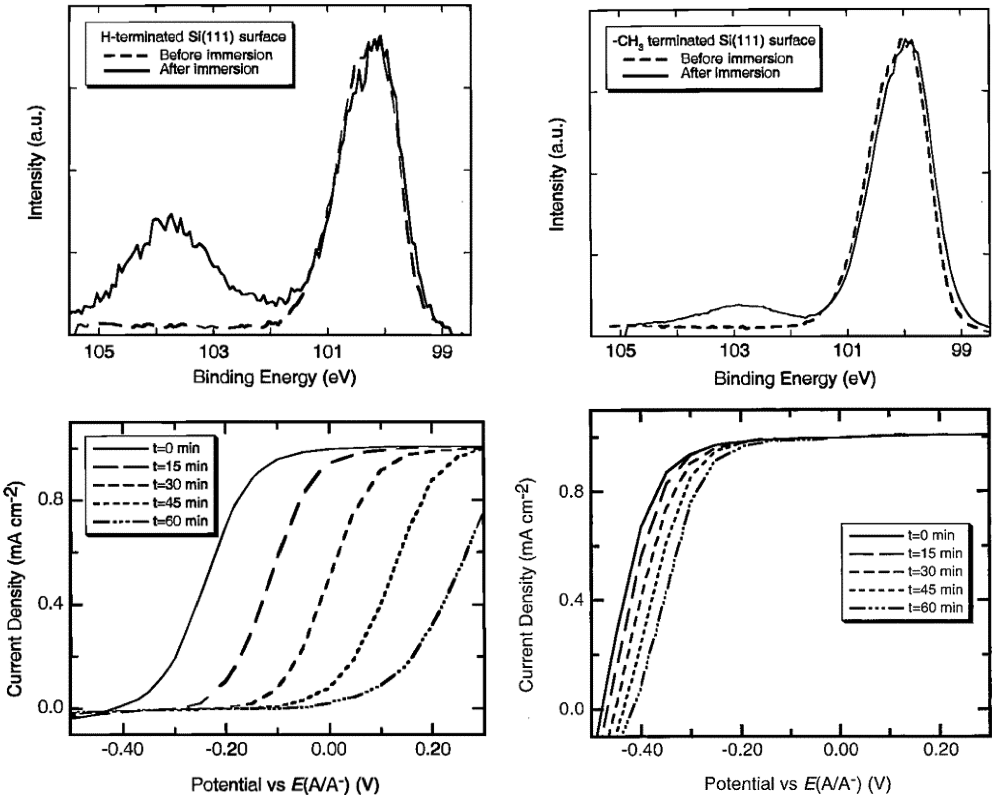

Figure 6. Top: high-resolution Si 2p XP spectra of H–Si(111) (left) and CH_3–Si(111) (right) before and after immersion in aqueous 0.35 M $K_4Fe(CN)_6$/0.05 M $K_3Fe(CN)_6$ for 10 min under ambient conditions. Bottom: time-dependent *J*–*E* data of H–Si(111) (left) and CH_3–Si(111) (right) in contact with $Fe(CN)_6^{3-/4-}$(aq) solution and illuminated with white light from an ELH-type tungsten-halogen bulb. The *J*–*E* data were collected at a scan rate of 50 mV s^{-1} in a three-electrode configuration versus a Pt wire reference electrode poised at the Nernstian potential of the redox couple, *E*(A/A^-). Adapted with permission from ref 45. Copyright 1998 American Chemical Society.

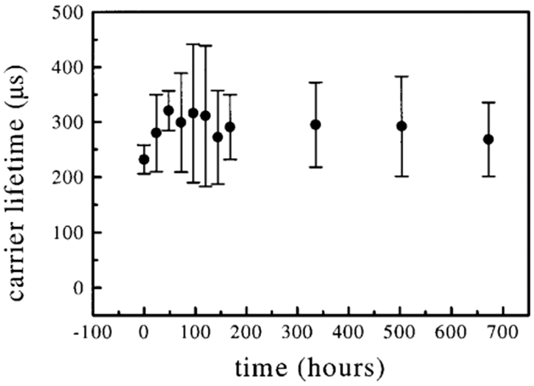

Figure 7. Mean carrier lifetimes for CH_3–Si(111) in contact with air. Samples were stored in air at room temperature in the dark between measurements. All measurements were performed with a light pulse sufficient to produce high-level injection during the initial carrier-decay dynamics. Error bars represent 1 standard deviation of the mean lifetimes. Reprinted with permission from ref 49. Copyright 2000, AIP Publishing LLC.

band gap for both H–Si(111) and CH_3–Si(111) surfaces,[50] consistent with the low *S* values observed on the macroscale on such surfaces and with the large open-circuit voltages obtained for *n*-Si/1,1′-dimethylferrocene$^{+/0}$/CH_3CN contacts.[51]

The band structure of CH_3–Si(111) has been deduced from high-resolution photoelectron spectroscopy data.[26] The results showed a 0.1 eV difference between the surface and bulk Fermi levels, corresponding to negligible band bending and indicating that nearly all of the surface states were passivated and electronically inactive. The results also showed that the methyl groups on the surface created a surface dipole of −0.4 eV. C_2H_5-terminated Si(111) has been shown to have a slightly smaller surface dipole of −0.23 eV and similarly low band bending.[32] Electrochemical measurements are consistent with the more negative surface dipole of the CH_3–Si(111) surface relative to the H–Si(111) surface: methylation shifts the band-edge positions of n- and p-Si(111) surfaces by −400 and −250 mV relative to H-terminated n- and p-Si(111), respectively.[51] Additionally, the band-edge positions of a Si electrode have been shown to be fixed with respect to pH by methyl termination, whereas a pH dependence would be expected for oxidized Si.[46,47]

Although methyl functionalization is expected to produce an increase in the series resistance to interfacial charge transfer relative to H–Si(111) surfaces,[44,45] the *J*–*E* behavior of CH_3–Si(111) surfaces in aqueous 10 mM methyl viologen^{2+} has been shown to follow the ideal model of electron transfer across a semiconductor/liquid junction (diode-quality factors of 1.1–1.3), whereas H–Si(111) surfaces quickly decayed to diode-quality factors of ~2.[46] Methyl termination of Si(111) can thus effectively inhibit oxidation in aqueous solutions while still allowing for electron transfer at the surface. Hg/Si contacts offer nearly ideal conditions for studies of charge-transfer energetics.[52] H–Si(111) and CH_3–Si(111) contacted with Hg both formed Schottky junctions, and the difference in the barrier heights, Φ_b, was consistent with the change in electron affinity (due to the surface dipole introduced by functionalization) measured in UHV. The current density vs voltage ($J-V$) behavior of Hg junctions formed on freshly prepared H−Si(111) and CH_3−Si(111) was compared to junctions formed on identically prepared surfaces that instead had been aged 24 h under ambient conditions before testing. The behavior of the Hg/CH_3−Si(111) junction was essentially independent of aging, whereas the Hg/H−Si(111) junction showed significant deterioration of the $J-V$ response after aging in ambient.

Metal/Si junctions formed by evaporation of Au or Cu on CH_3−Si(111) form metal silicides, as shown by XPS.[53] Schottky junctions are also formed in these experiments, but the measured Φ_b values were identical to those for the same metals on nonpassivated Si(111)-(7 × 7), and were not larger than the Φ_b value of these metals evaporated on H−Si(111). In another study, electrodeposition of Cd and Pb was used to avoid silicide formation under ambient conditions, and both metals were electrodeposited with no oxidation of the Si detectable by high-resolution XPS.[54] Unlike for evaporated Au and Cu, the Φ_b values of the Schottky junctions were larger for the metal/CH_3−Si(111) junctions than for the metal/H−Si(111) junctions, in accord with expectations for the sign and magnitude of surface dipole introduced by methylation, as revealed by the UHV studies.

V. BEYOND METHYL-TERMINATED Si(111)

This Account has primarily discussed methyl-terminated Si(111) and provides comparisons to the behavior of H−Si(111) surfaces. Recent work has increasingly focused on looking beyond simple methyl or alkyl termination to methods that enable functionalization with chemically active species, for example, molecular catalysts, seed layers for atomic layer deposition, or chemical or biological sensors, while maintaining the chemical and electronic passivation afforded by Si−C functionalization of essentially all surface atoms.

A number of secondary functionalization methods for alkylated, oxide-free Si have been demonstrated, including covalent attachment of polymer films and small molecules by reaction with allyl-terminated Si(111);[33,55] Heck coupling of olefins to thienyl-modified Si(111);[37] Suzuki, Heck, and Sonogashira coupling of alkene-, alkyne-, and halide-terminated surfaces;[56] azide "click" chemistry on ethynyl−Si(111);[57] and atomic layer deposition on self-assembled monolayers formed by hydrosilylation.[58,59] Recent work has leveraged the small size of methyl groups to "fill in" unalkylated sites after surface modification with bulkier groups used for secondary functionalization (e.g., thienyl or allyl).[37,47,60,61] The resulting mixed monolayers exhibited surface coverages, oxidation rates, and S values comparable to those of CH_3−Si(111), while still containing reactive moieties that may be utilized for secondary functionalization. Ethynyl- and propynyl-terminated Si(111) surfaces have also been synthesized, but have not yet been characterized with the same level of detail as the CH_3−Si(111) surface.[30,52] These groups are expected to be able to cover 100% of Si(111) surface atoms, like methyl termination, but the presence of an unsaturated bond may enable secondary functionalization.[57] Mixed monolayers and other surface termination schemes offer the potential to use the chemical and electronic passivation afforded by forming Si−C bonds while enabling additional modification of the surface. This area is one of the major focal points of ongoing research in semiconductor functionalization.

The two-step halogenation/alkylation method has also been applied to Si(100)[62] and Ge(111)[63,64] surfaces, and in both cases alkylation has been achieved with little or no oxidation of the substrate. CH_3−Si(100) was shown to have a low surface recombination velocity ($S = 30 \pm 10$ cm s^{-1}), and oxidation in air was greatly reduced from that of H-terminated Si(100), although not to quite the same extent as CH_3−Si(111). CH_3−Ge(111) samples exhibit surface recombination velocities < 100 cm s^{-1}. Field-dependent surface recombination velocity measurements indicated that methyl-terminated n-type Ge(111) had a surface potential near 300 mV and such surfaces formed a rectifying junction in contact with Hg. Although additional characterization of the structure, chemical passivation, and electronic characteristics of these surfaces is warranted, these studies demonstrate that the halogenation/alkylation chemistry can be applied beyond Si(111). Likewise, numerous improvements can likely be realized by further tailoring the chemistry to the specific surface, each of which presents its own challenges, for example, the formation of mono-, di-, and trihydrides on HF-etched Si(100) and the lack of wet-etching methods that form atomically smooth Si(100) or Ge(111).

VI. SUMMARY AND OUTLOOK

The extensive research regarding methyl-terminated Si(111) has brought to light many details of the structure, chemistry, and electronic properties of this surface. When prepared by halogenation/methylation, essentially 100% methylation of surface Si atoms can be achieved on large, flat terraces, yielding a surface that is closely analogous to H−Si(111). Yet the CH_3−Si(111) surface has been shown to provide improved chemical passivation compared to H−Si(111) under ambient conditions and, in many cases, under electrochemical conditions. Methylation also provides excellent electronic passivation of the Si(111) surface, with relatively long charge-carrier lifetimes and low surface recombination velocities. However, perhaps more important is the combination of this electronic passivation with the chemical passivation that enables these benefits to be realized over extended periods of time under conditions that will be experienced in real-world devices. CH_3−Si(111) certainly is not a replacement for H−Si(111) (after all, H−Si(111) is a starting point for the two-step halogenation/alkylation scheme), but the studies described in this Account demonstrate that CH_3−Si(111) has many potential applications beyond what is possible with hydrogen termination.

While the chemical passivation afforded by methylation is impressive, many applications require the ability to do further chemistry at the surface while maintaining the electronic passivation and resistance to oxidation of CH_3−Si(111). Opportunities exist to increase the utility of Si−C functionalization, for example, by developing robust secondary functionalization methods, and to improve the understanding of the detailed surface chemistry and surface structure of mixed monolayers employed in several secondary functionalization schemes. The negative surface dipole imparted by methylation effectively decreases the electron affinity of the CH_3−Si(111) surface, but additional surface-modification methods are needed to control the magnitude and sign of the surface dipole to thereby control the band alignment and interfacial charge transfer at a variety of semiconductor/liquid or semiconductor/metal junctions. Perhaps one of the greatest challenges for widespread application of methyl termination of Si is the extension of current knowledge to other crystal faces and less homogeneous and well-defined surfaces, the topic of comparatively few studies. Although some applications may be able to take advantage of the terraced $CH_3-Si(111)$ surface, many other applications will emerge if similar benefits can be achieved on other surfaces. In this respect, the detailed studies of methyl-terminated Si(111) surfaces of the past two decades are the foundation for an emerging field of deliberate chemical control of semiconductor interfaces through chemical modification of such surfaces.

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Notes

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