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Covalent Attachment of Acetylene and Methylacetylene Functionality to Si(111) Surfaces: Scaffolds for Organic Surface Functionalization while Retaining Si−C Passivation of Si(111) Surface Sites

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Covalent attachment of organics to Si has attracted much attention, due to the ability to passivate the Si surface toward chemical oxidation while retaining desirable electrical properties.[1] Functionalization methods include alkyl-Grignard or alkyllithium reagents,[2] hydrosilylation,[3−5] electrochemical grafting,[6,7] and mechanochemical functionalization.[8] Due to steric constraints, olefin addition to surface Si−H bonds,[9] as well as most other radical-based functionalization reactions, cannot effect complete Si−C-type termination of the atop sites on the Si(111) surface. The distance between Si atop sites on an unreconstructed 1 × 1 Si(111) surface is 3.8 Å,[10] whereas the van der Waals diameter of methylenes in alkyl groups has been estimated to be 4.5−5.0 Å.[9,11] Hence functionalization with alkenes or long chain alkyls necessarily leaves Si atoms that are not bonded to carbon, with some suggestions that the remaining Si atoms are terminated with −OH groups,[4] with −H,[12,13] or with unidentified bonding states. These sites, in turn, may be oxidized or lend otherwise undesirable chemical or electrical properties to the resulting Si surfaces. Complete coverage of Si atop sites has been achieved by CH_3 termination of Si(111), through a two-step chlorination/Grignard process.[2,14] This approach produces surfaces that are highly passive both chemically and electrically.[15,16] The van der Waals diameter of a $-CH_3$ group is 2.3 Å,[17] and packing in a 1 × 1 arrangement is thus feasible for CH_3-terminated Si(111) surfaces.

Methyl termination does not, however, readily facilitate elaboration of the passivated CH_3−Si(111) surface through subsequent chemical reactions. The ability to directly attach controlled functionality to a fully passivated, Si−C-bonded, surface is highly desirable for numerous applications, including biosensing[18−20] (where an intervening oxide dielectric layer will screen most of the charge and reduce the sensitivity of the system), forming molecular-level contacts,[21] obtaining facile electron tunneling through unsaturated organic species connected directly to the Si surface,[22] molecular level interconnects and gates to Si nanowires,[23] and similar applications. We describe herein a functionalization process which allows complete passivation of the Si(111) surface sites with Si−C bonds, while also providing a scaffold for further, facile, functionalization of the Si surface.

Molecular modeling indicates that termination of atop sites on Si(111) surfaces with Si−C≡C−R-type species, where R = H or CH_3, can proceed to complete coverage with essentially no bond strain.[24] With R = CH_3, the surface so obtained is closely related to the CH_3-terminated Si(111) surface, except that the methyl packing is displaced vertically by a linear, sp-hybridized, Si−C≡C− unit from the surface plane. With R = H, the reactivity of the surface-bound alkyne can be used as a scaffold to effect further surface modification, while still providing full termination of the surface Si−C bonds even for overlayer groups that can sterically only react with a limited number of sites on the surface. The desired Si−C≡C−R functionality cannot be introduced by Si−H radical reactions with olefins, but can readily be achieved by reaction of Na acetylides with a halogenated Si(111) surface, through a straightforward extension of the two-step Si chlorination/alkylation process.[2]

H-terminated Si(111) surfaces were produced by etching cleaned, oxidized Si(111) samples in degassed 40% NH_4(aq). The H−Si(111) surfaces were then converted into Cl−Si(111) surfaces by treatment with PCl_5 in chlorobenzene, with benzoyl peroxide added as a radical initiator.[2] The Cl−Si(111) surfaces were then exposed under anaerobic conditions to solutions of either NaC≡CH or NaC≡C−CH_3 in tetrahydrofuran (THF), rinsed with CH_3OH and then THF, and dried with N_2(g). The resulting surfaces were characterized by X-ray photoelectron spectroscopy (XPS),[2] multiple internal reflection infrared (ATR−IR) spectroscopy, charge-carrier lifetime measurements,[16] and electrochemistry.[25]

Survey scan XPS data on either the NaC≡CH- or NaC≡C−CH_3-treated Si surfaces showed the complete disappearance of Cl, no Na, and appearance of C 1s and O 1s signals, in accord with the behavior of Cl−Si(111) surfaces exposed to Grignard or organolithium reagents.[2] A high-resolution scan of the Si 2p region (Figure 1A, a) showed no evidence for oxidized Si. A high-resolution of the C 1s region (Figure 1B) showed three emissions, at 285.2, 284.0, and 286.6 binding eV, respectively. The 284.0 eV emission has been ascribed to a carbon bonded to the less electronegative Si.[26−28] The ratio of this unique C−Si peak to the Si 2p peak area can provide quantitative information on the amount of C covalently bonded to Si, provided that a suitable reference system is available.[26−28] A suitable reference system is the CH_3−Si(111) surface, which has been shown to produce complete Si−C termination by low-energy electron diffraction,[28] soft XPS,[13] IR,[12] and scanning tunneling microscopy (STM)[14] studies. The C_{Si}/Si 2p peak area ratio for the Si−C≡CH surface was 90 ± 10% of that for CH_3−Si(111), whereas the ratio for Si−C≡C−CH_3 termination was 105 ± 10% of that for CH_3−Si(111). For comparison, C_2H_5-terminated Si(111) shows a C_{Si}/Si 2p peak ratio of 90 ± 20% relative to CH_3−Si, octyl-terminated Si(111) shows a peak ratio of 60 ± 10%, and isopropyl-terminated Si(111) shows a peak area ratio of 40 ± 20% relative to CH_3−Si(111) surfaces.[29]

Figure 2A displays a portion of the infrared spectrum, relative to a SiO_2-covered Si(111) surface, of the surface obtained by treatment of Cl−Si(111) with NaC≡CH. A band appeared at 2179 cm^{-1}, assignable to the weak C≡C stretching band of the alkyne functionality.[30] The band was polarized normal to the surface plane (Figure 2A). The Si surface infrared spectrum has also been shown to be diagnostic of residual Si−H surface bonds, to the level of <0.1 monolayer, from reactions that do not terminate every Si atop site, such as $-C_2H_5$, phenyl, and other alkyl groups.[12] Labeling studies have shown that the residual Si−H arises from reaction

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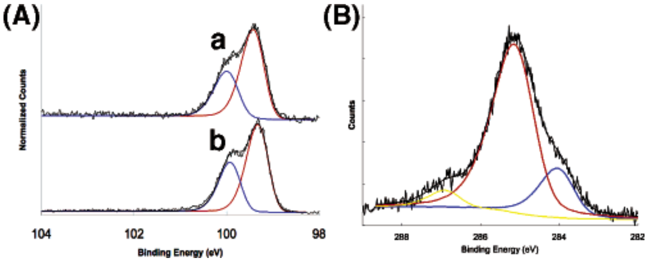

Figure 1. (A) Si 2p XPS of Si surfaces. (a) $Si-C\equiv C-H$- and (b) $Si-C\equiv C-H$-terminated surface further functionalized by exposure to *n*-C_4H_9-Li followed by exposure to *para* $Br-C_6H_5-CF_3$. Black = data; red, blue = fits to Si 2p doublet. (B) XPS of C 1s region, showing C−Si (blue), C−C (red), and C−O (yellow) peaks for $Si-C\equiv C-H$. Data are in black.

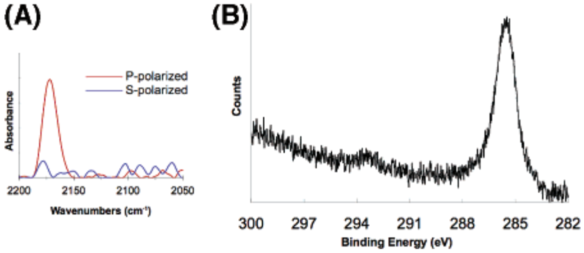

Figure 2. (A) IR of $Si-C\equiv C-H$. (B) XPS of C 1s region for $Si-C\equiv C-C_6H_5CF_3$ showing F-shifted C at 294 eV.

with the THF solvent at sites that cannot be readily alkylated due to steric constraints.[25] The IR spectra of surfaces functionalized with $-C\equiv CH$ or $-C\equiv C-CH_3$ groups exhibited no detectable Si−H stretch, in accord with observations for CH_3-terminated Si(111) surfaces,[12] providing additional evidence for the complete termination of the surface with alkyne groups.

Electrochemical studies provided further evidence for the lack residual Si−H bonds to the alkyne-terminated Si(111) surfaces. In water, the H−Si(111) surface exhibits a characteristic Si−H oxidation at −0.7 V vs SCE.[25] CH_3-terminated Si(111) surfaces show negligible anodic current at this potential, whereas C_2H_5-Si(111) and other surfaces with residual Si−H bonding show oxidative currents that correlate with the amount of Si−H on the surface.[25] Si(111) surfaces functionalized with either $-C\equiv CH$ or $-C\equiv C-CH_3$ groups showed negligible anodic current in this range, providing further evidence that no Si−H bonds are present and that the surfaces are fully Si−C terminated.

Such surfaces show excellent electrical properties, with surface charge carrier recombination velocities, S, determined by radio frequency conductivity methods[16] of $(6 \pm 1) \times 10^1$ cm s^{-1} for the $-C\equiv C-CH_3$-functionalized Si surfaces. These measurements indicate that these surfaces possess less than one electrically active defect site in every one million surface atoms, assuming a geometric cross section for the trap sites on the surface.[31] The low surface recombination velocities persisted for at least 20 days upon exposure to ambient air, with no oxidation detectable by XPS.

Functionalization of the $-C\equiv CH$-terminated Si(111) surface was demonstrated by introduction of *para* $-C_6H_5CF_3$ groups. The $-C\equiv CH$-terminated surface was exposed to 2.5 M *n*-C_4H_9Li in hexanes, the surface was rinsed with hexanes and then exposed to 4-$Br-C_6H_5CF_3$. XPS in the C 1s region showed an emission at 294 binding eV that is characteristic of carbon in trifluoromethyl groups.[32] The ratio of this C 1s signal to the F 2p signal, after correction for the different sensitivity factors of the C 1s and F 2p emissions, was 1:2.8, consistent with the introduction of $-CF_3$ groups onto the surface. Relative to the Si 2p area, the 285.2 eV C 1s signal increased by 40% upon functionalization relative to the $Si(111)-C\equiv CH$ surface. The coverage of $-C_6H_5CF_3$ groups was calculated to be 0.35 ± 0.10 monolayers, as obtained from the ratio of the 294 eV C 1s emission to the Si 2p emission, using the appropriate sensitivity factor ratio and escape depth of Si 2p photoelectrons for Al Kα excitation. No oxide in the Si 2p region was detectable on this surface (Figure 1A, b).

In summary, Si(111) surfaces have been terminated with acetylenic functionality, which sterically allows both full Si−C termination of atop sites on a Si(111) surface and provides a reactive functionality for further chemical modification of the Si surfaces. The introduction of conjugated moieties offers the possibility of introducing well-defined “molecular wires” between Si surfaces and other functional groups or nanostructures, whereas the ability to react the Si further with other organic[33] or inorganic groups opens up routes to Si functionalization while preserving the desirable chemical and electrical properties of full Si−C atop site termination on the Si(111) surface.

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