Alkylation of Si Surfaces Using a Two-Step Halogenation/Grignard Route

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Despite the fact that H-terminated, HF-etched Si crystals are the starting point for construction of most contemporary electronic devices,[1] little is known about the chemical reactions of H-terminated Si surfaces under ambient temperature and pressure.[2,3] Functionalization of Si without partial oxidation and/or formation of electrical defects is potentially important in fabricating improved electronic devices[4,5] as well as in measurement of charge transfer rate constants at semiconductor/liquid contacts.[6] One recently described approach involves the reaction of HF-etched Si(111) with olefins and organic diacyl peroxides, in which formation of a self-assembled (near)-monolayer of Si-alkyls was hypothesized.[2] We report here an alternative strategy to functionalize HF-etched Si surfaces involving halogenation and subsequent reaction with alkyl Grignard or alkyl lithium reagents. We report vibrational spectroscopic and temperature programmed desorption data which confirm that the alkyl groups are bonded covalently to the Si surface, and we demonstrate that such overlayer formation can impede the undesirable oxidation of Si in a variety of environments while providing surfaces of high electrical quality.

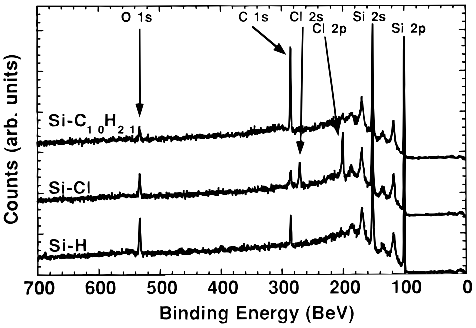

Figure 1. X-ray photoelectron survey spectra of H-terminated, chlorinated and $-C_{10}H_{21}$ terminated Si(111) surfaces. The main peaks observed are O 1s (532 BeV), C 1s (284.6 BeV), Cl 2s (270 BeV), Cl 2p (199 BeV), Si 2s (151 BeV), and Si 2p (100 BeV). All peak positions were normalized to that of the C 1s peak, which was taken to be at 284.6 BeV.

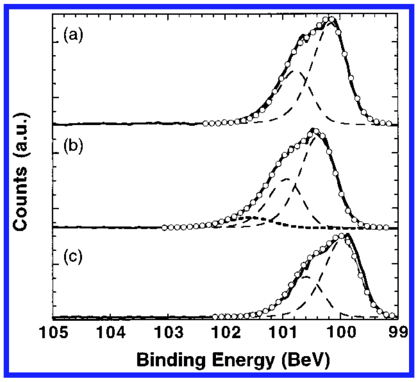

Figure 2. High-resolution XP spectra of the Si 2p region of H-terminated, chlorinated, and $-C_{10}H_{21}$ terminated Si(111) surfaces. The solid lines are the data, the dashed lines are the deconvolutions, and the open circles are the resulting fits to the spectrum. (a) The H-terminated Si surface yielded a signal that was well-fit to a spin−orbit doublet of Si $2p_{3/2}$ and Si $2p_{1/2}$ in the expected 2:1 area ratio, 0.60 eV energy separation, and peak position for lattice Si.[24] (b) In accord with expectations for surficial Si−Cl bonds,[10] chlorination produced an XPS spectrum which could only be well fit by including a third peak at 0.98 eV higher energy than the Si $2p_{3/2}$ peak, while holding the parameters of the substrate doublet constant. (c) Alkylation produced a Si 2p spectrum that was well-fit to the same spin−orbit doublet obtained for the H-terminated Si surface. The chemical shifts of the Si−H and Si−C bonds are too small to observe relative to lattice Si atoms. No oxidized Si, which would appear between 101 and 103.5 BeV, can be detected in the Si 2p region (<0.05 monolayer) in either a or c, confirming prior reports that the O 1s signals observed on HF-etched Si samples exposed to ambient air and/or organic solutions in Figure 1 arise from adventitious carbonaceous material and do not indicate the formation of Si oxides or alkoxides.[24,25]

The H-terminated Si surface[7] was first exposed to PCl_5 for 20−60 min at 80−100 °C, in chlorobenzene with benzoyl peroxide as the radical initiator.[8,9] Upon chlorination, the XP survey spectra (Figure 1) showed peaks at 270.2 ± 0.4 binding electron volts, BeV, (Cl 2s) and 199.3 ± 0.4 BeV (Cl 2p), indicating that this procedure yielded Cl on the surface. The high-resolution XP spectrum of the Si 2p peak of this surface displayed, in addition to the substrate Si signal, an additional peak located at 0.98 ± 0.12 BeV higher in binding energy (Figure 2) whose position and intensity was consistent with the formation of a surface Si−Cl bond.[10] Auger electron spectra (AES) also confirmed the presence of Cl on the silicon surface. High resolution electron energy loss spectra (HREELS) of this surface exhibited a characteristic peak at 560 cm^{-1} that was not present on the H-terminated Si surface, confirming the formation of covalent Si−Cl bonds at the surface.[11] Temperature programmed desorption spectra of the chlorinated surface showed dominant signals at 64 (SiCl), 71 (Cl_2), and 135 ($SiCl_3$) amu, peaking at 670 and 850 K, which is characteristic of chlorinated silicon surfaces.[10,12] The 560 cm^{-1} peak in the HREELS and the Cl peak in the AES disappeared following thermal desorption.

Exposure of the chlorinated Si surface to alkyl-Li (RLi: R = C_4H_9, C_6H_{13}, $C_{10}H_{21}$, $C_{18}H_{37}$) or alkyl-Grignard (RMgX: R

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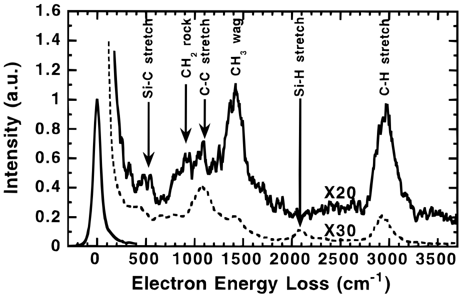

Figure 3. High-resolution electron energy loss (HREEL) spectra of a Si$-C_2H_5$ surface. The solid line displays a representative spectrum obtained from an "as derivatized" surface before thermal desorption, and the dashed line represents the spectrum obtained after heating the surface to 600 K. The fwhm of the Si elastic peak was 11 meV (88 cm^{-1}). Both spectra were collected at a substrate temperature of 80 K.

= CH_3, C_2H_5, C_4H_9, C_5H_{11}, C_6H_{13}, $C_{10}H_{21}$, $C_{12}H_{25}$, $C_{18}H_{37}$; X = Br, Cl) reagents[13] for 30 min to 8 days (depending on the chain length of the alkyl group) at 80 °C produced the desired functionalized Si surfaces. XP survey spectra of these surfaces[14] showed only Si, C, and O signals, with little or no detectable Li (or Mg) or halide peaks. The C/Si ratio in the XPS survey scan increased monotonically when the chemistry was performed with reagents of increasing chain lengths ($-C_nH_{2n+1}$ with $2 \leq n \leq 12$). Moreover, the high binding energy peak observed in the Si 2p region of the chlorinated surface disappeared upon alkylation. On these alkylated surfaces, no oxidation of silicon was detectable by XPS and the Si 2p spectra were identical to those observed for H-terminated Si(III) surfaces.

Vibrational spectroscopy and temperature programmed desorption measurements were consistent with the formation of covalent Si$-$C bonds of chemisorbed alkyls on the functionalized Si surface. Multiple-internal-reflection Fourier-transform infrared (MIR-FTIR) spectroscopy on the surfaces functionalized with $-C_{18}H_{37}$ and $-C_{12}H_{25}$ yielded asymmetric methylene C$-$H stretching peaks (ν_a) at 2917 and 2914 cm^{-1}, respectively (fwhm = 16 ± 2 cm^{-1}). These peak positions for alkylthiol monolayers on Au surfaces have been interpreted to indicate a highly crystalline environment of the alkyl chains.[15,16] High-resolution electron energy loss spectroscopy (HREELS) performed on the $-C_2H_5$ functionalized Si surface[17] (Figure 3) showed a peak for the C$-$H stretching mode at 2900 cm^{-1}, the CH_3 umbrella (wag) mode of the terminal methyl group at 1400 cm^{-1}, the C$-$C stretching mode at 1100 cm^{-1}, the CH_2 rocking mode at 900 cm^{-1}, and a peak at 510 ± 50 cm^{-1} which is assigned to the Si-C stretching mode.[18,19] All these vibrational peaks were either significantly reduced or disappeared completely after a temperature programmed desorption, which produced mass spectrometric signals at 28 and 27 amu that were consistent with the fragmentation pattern of ethylene. The appearance of the Si$-$H stretching peak at 2090 cm^{-1}, the Si$-$H bending mode at 700 cm^{-1}, and the reduction in the CH_3 umbrella (wag) mode at 1400 cm^{-1} after heating the Si$-C_2H_5$ surface to 600 K were consistent with a β-hydride elimination process evolving ethylene from an ethyl-terminated surface (Figure 3).[20,21] The chemical and spectroscopic data described herein are therefore entirely consistent with the desired alkylation chemistry on the Si surface.[22] The Si surface reaction chemistry elucidated herein is similar to the reaction of hindered model silanes such as 1,1,2,2-tetramesityldisilane, which undergo chlorination during reaction with PCl_5 or other chlorinating agents[9] and conversion of chlorosilanes using Grignard or organolithium species to Si-alkyls.[13]

These alkylated overlayers impeded the rate of surface oxidation of the Si. As measured by the Si 2p region of the XP spectra, the H-terminated Si(111) surface formed half a monolayer of oxide after 3 h in air. In contrast, the $-CH_3$ functionalized surface showed half a monolayer of oxide after 5 h of exposure to air. Si surfaces derivatized with longer alkyl chains were even more resistant to oxidation, and some did not reach half monolayer oxide coverage even after 2 days of exposure to air. This result is significant because adventitious oxidation of H-terminated Si degrades the electronic properties of the surface.[5] Additional stability tests on the robustness of the overlayer were performed by immersing the surface in boiling aerated chloroform for 15 min and then in boiling aerated water for another 15 min.[2] The constant C/Si ratio in the XPS before and after exposure to the solvents indicated that the overlayer was not removed even under these conditions. The electrical properties of these surfaces were evaluated in contact with 1,1′-dimethylferrocene$^{+/0}$ in methanol by steady state current$-$voltage measurements under illumination.[23] The open circuit voltages, which are a measure of the rate of surface recombination of defective surfaces, were similar for the H-terminated and the alkylated Si surfaces and indicated less than one defect in every 10^5 surface atoms under these conditions.

The two-step reaction sequence described above, radical-initiated chlorination followed by reaction with Grignard or organolithium reagents, thus appears to provide a simple, general approach to functionalization of the H-terminated Si surface. This procedure has allowed formation of surface functionalities not available through other currently known routes, such as methylated Si surfaces. These results confirm that for the technologically important silicon surface, passivation to oxidation can be achieved without compromising its electrical characteristics.

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