Modification of Si(111) Surfaces with Covalently-Attached Alkyl Chains

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A procedure has been developed that facilitates the functionalization of (111)-oriented Si surfaces with alkylating reagents. The two-step procedure involves radical initiated chlorination of the Si surface with PCl5 followed by reaction of the chlorinated surface with alkyl-Grignard or alkyl-lithium reagents. The surface chemistry that accompanies these reaction steps has been investigated using x-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), temperature programmed desorption (TPD), high resolution electron energy loss spectroscopy (HREELS), infrared spectroscopy (IR) in both glancing transmission (TIR) and attenuated total multiple internal reflection (ATR) modes, ellipsometry and contact angle goniometry. The XPS data show the appearance of the Cl signal upon chlorination and show its removal and concomitant appearance of a C 1s signal after the alkylation step. Auger electron spectra, in combination with TPD spectroscopy, demonstrate the presence of Cl after the chlorination process and its subsequent loss after thermal desorption of Si-Cl fragments on heating the Si surface to 1200 K. High resolution XP spectra of the Si 2p region show an additional component peak on deconvolution coresponding to Si-Cl bond formation after the chlorination step, and subsequent disappearance of this component after the alkylation step. IR spectra show the loss of the perpendicularly-polarized 2083 cm-1 silicon-monohydride (Si-H) vibration after the chlorination step, while HREELS spectra show the appearance of vibrations due to Si-Cl stretches upon chlorination of the Si surface. Furthermore, the HREELS spectra show the disappearance of the Si-Cl stretch and the appearance of an Si-C vibration at 650 cm-1 after alkylation of the Si surface. Ellipsometric measurements show that the thickness alkyl overlayer varies monotonically with the length of the alkyl group used in the reactant. Contact angle and IR measurements indicate that the packing of alkyl groups in the monolayers is less dense than that found in alkylthiol monolayers on Au. As determined by XPS, the alkylated surfaces show enhanced resistance to atmospheric oxidation and to various wet chemical treatments, compared to the H-terminated Si surface. The two step reaction sequence thus provides a simple, well-characterized, and apparently general approach to functionalization of (111)-oriented, H-terminated silicon surfaces using wet chemical methods that also preserves the low electrical defect density of the H-terminated Si surface.

In addition, the reaction chemistry of H-terminated crystalline Si(111) and Si(100) surfaces in CH3OH, CD3OD, CF3(CH2)3OH, C4H9OH and C4D9OD solutions containing FcBF4, I2, or Br2 was monitored using X-ray photoelectron (XP) spectroscopy and infrared (IR) spectroscopy. Addition of the one-electron oxidant Fc+, or addition of the oxiding species I2 or Br2, produced diagnostic changes in the IR spectra that clearly indicated formation of surficial Si-OR groups. XPS data confirmed the conclusions of the IR studies. Under our reaction conditions, no detectable reaction occurred without the presence of the oxidant. The data are consistent with oxidative activation of the surficial Si-H bonds towards nucleophilic attack by the alcohols. The reaction chemistry was generally similar on (111)- and (100)-oriented Si surfaces, although some differences were observed in the ratio of reaction products on the two different surface orientations. Alkoxylated surfaces were also prepared by a two-step process in which the surface was first chlorinated and then reacted with LiOCH3, LiOCD3, or LiO(CH2)3CF3. The data indicate that formation of Si-X bonding alone is not sufficient to provide a robust correlation between the electronic and chemical properties of such crystalline Si surfaces, and that formation of Si-alkoxyl bonds is a common motif for surfaces often used in electronic and electrochemical studies of Si.