

Stabilization of Si Photoanodes in Aqueous Electrolytes through Surface Alkylation

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A two-step chlorination/alkylation method was used to introduce $-\text{C}_n\text{H}_{2n+1}$ ($n = 1-6$) functionality onto single-crystal, (111)-oriented, n-type Si surfaces. H-terminated Si photoanodes were unstable under illumination in contact with an aqueous 0.35 M $\text{K}_4\text{Fe}(\text{CN})_6$ –0.05 M $\text{K}_3\text{Fe}(\text{CN})_6$ electrolyte. Such electrodes displayed low open-circuit voltages and exhibited a pronounced time-dependent deterioration in their current density vs potential characteristics due to anodic oxidation. In contrast, Si surfaces functionalized with $-\text{CH}_3$ and $-\text{C}_2\text{H}_5$ groups displayed significant improvements in stability while displaying excellent electrochemical properties when used as photoelectrodes in the aqueous $\text{Fe}(\text{CN})_6^{3-/4-}$ electrolyte.

Semiconductors having band gaps between 0.9 and 1.7 eV are well-known to be optimal for use in photoelectrochemical solar energy conversion devices.^{1,2} Si, with a band gap of 1.12 eV, is an especially attractive material for this application. The hydrogen-terminated Si surface obtained from wet chemical etching with $\text{HF}(\text{aq})$ is nearly electrically perfect when initially formed,^{3,4} but this surface readily oxidizes in air or in water-containing ambients. The oxide not only introduces electrical defect states but also forms an insulating, passivating overlayer that quickly prevents photocurrent flow through an electrochemical cell.^{5–8}

At present, there is no general strategy for stabilizing Si electrodes in aqueous media. The surface of Si electrodes has been coated previously with islands or films of metal.^{9–15} This process creates electrically undesirable buried Si/metal junctions on protected regions of the electrode. Introduction of functional groups onto the Si surface through silanization chemistry has been demonstrated to enhance the stability of Si electrodes at low light levels in water with certain redox species,^{7,16–18} but the electrical quality of the surface was sacrificed owing to the need for a thin native oxide layer on the surface to facilitate the functionalization process. Crystalline Si surfaces have been recently functionalized by chlorination/alkylation¹⁹ or radical-based olefin addition methods.^{20,21} We report herein that silicon surfaces derivatized with covalently attached alkyl chains, using the chlorination/alkylation procedure, have outstanding electrochemical properties in contact with an aqueous $\text{Fe}(\text{CN})_6^{3-/4-}$ electrolyte. Furthermore, surfaces derivatized through the use of such covalent Si–C linkages exhibit significantly more stable photoelectrochemical performance than has been observed for H-terminated Si electrodes.

The (111)-oriented n-type Si single crystals used in this work were first HF -etched^{3,4} and then chlorinated for 40–50 min at 90–100 °C in a 0.6–0.7 M solution of PCl_5 in chlorobenzene, with benzoyl peroxide added as a radical initiator.¹⁹ Exposure of the chlorinated Si surfaces to alkyl Li (RLi : $\text{R} = \text{C}_4\text{H}_9$, C_6H_{13}) or alkyl Grignard (RMgBr : $\text{R} = \text{CH}_3$, C_2H_5) reagents for 4–12 h at 65–80 °C produced the desired, alkylated Si surfaces. This procedure has been shown by a variety of methods, including X-ray photoelectron spectroscopy (XPS),

infrared spectroscopy, and high-resolution electron energy loss spectroscopy (HREELS), to produce surficial Si–C bonds.¹⁹

Figure 1a depicts the high-resolution XP spectrum that was observed after a H-terminated n-type Si(111) electrode had been placed in contact with 0.35 M $\text{K}_4\text{Fe}(\text{CN})_6$ –0.05 M $\text{K}_3\text{Fe}(\text{CN})_6$ (aq) for 10 min at room temperature. The Si 2p XPS peak ratios indicate that approximately three monolayers of oxide were produced on the Si surface during this immersion step, even though negligible light-induced current had passed through the interface. As displayed in Figure 1b, the first electrochemical current density (J) vs potential (E) scan of this surface, at a light intensity sufficient to produce a short-circuit photocurrent density of 1.0 mA cm^{-2} , showed a sigmoidally-shaped curve with a low open-circuit voltage (V_{oc}) and a low fill factor for conversion of incident light into electrical energy. Thus, the electron–hole pairs produced by illumination of the Si resulted in an anodic photocurrent that oxidized the Si surface. Subsequent scans displayed further deterioration in the performance of the electrode with time. Even though this electrolyte solution contained >0.3 M of the hole scavenger $\text{Fe}(\text{CN})_6^{4-}$, oxidation of Si competed effectively with hole scavenging by the redox couple.

Figure 2a depicts a high-resolution XP spectrum for a Si electrode that had been modified by treatment with PCl_5 and then with CH_3MgBr . After immersion in the $\text{Fe}(\text{CN})_6^{3-/4-}$ solution for 10 min at room temperature, the XP spectrum of this surface showed less than one monolayer of oxide (Figure 2a). In contrast to the H-terminated Si surface, the initial J – E curve of this electrode showed negligible hysteresis and good rectification with a high fill factor (Figure 2b). For comparison, n-Si/Au Schottky contacts only produce $V_{\text{oc}} = 0.23$ V at these light intensities,^{22,23} and n-Si photoanodes coated with a thin native oxide and then modified with chlorosilylferrocene reagents only produce $V_{\text{oc}} = 0.30$ V in contact with the $\text{Fe}(\text{CN})_6^{3-/4-}$ electrolyte.⁷ Negligible Mg could be detected on the functionalized Si surfaces by XPS, and the photovoltage of the functionalized Si/liquid contact is higher than that for any known direct n-Si/metal contact (owing to the presence of Fermi level pinning at Si/metal contacts).^{1,22,24–26} Thus, the electrochemical properties of this system cannot be ascribed to the formation of a semiconductor/metal Schottky barrier from

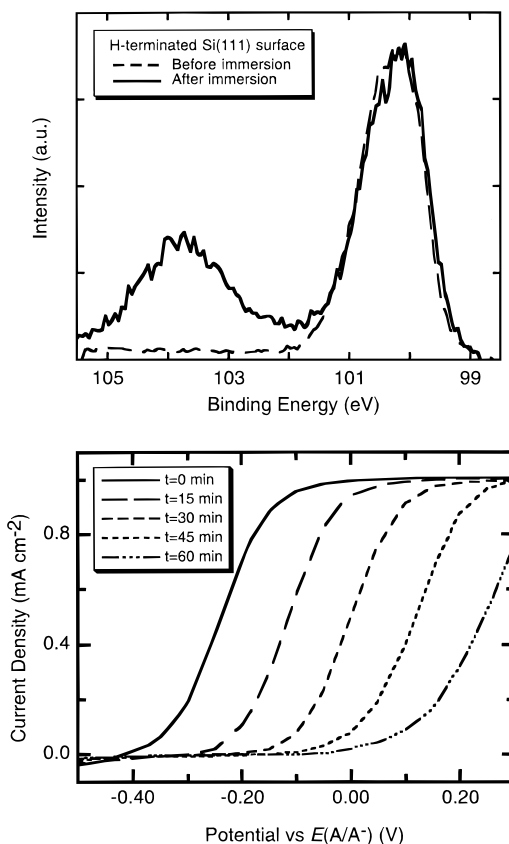


Figure 1. (a) High-resolution XP spectra of the Si 2p region of a H-terminated n-type Si(111) surface before and after immersion in 0.35 M $\text{K}_4\text{Fe}(\text{CN})_6$ –0.05 M $\text{K}_3\text{Fe}(\text{CN})_6$ (aq) solution for 10 min under ambient conditions. The $\text{Fe}(\text{CN})_6^{3-/4-}$ -exposed surface shows approximately three monolayers of oxide, as evidenced by the area of the peak that occurs at 3.6 eV higher in binding energy than the bulk silicon 2p peak. (b) Time-dependence of the J – E behavior of a H-terminated Si electrode in contact with $\text{Fe}(\text{CN})_6^{3-/4-}$ (aq) solution. The J – E curves were collected at a scan rate of 50 mV s^{-1} , and potentials were recorded in a three-electrode potentiostatic configuration vs a Pt wire reference electrode that was poised at the Nernstian potential of the redox couple, $E(\text{A}/\text{A}^-)$. The Si electrode was illuminated with the white light output of an ELH-type tungsten–halogen bulb.

residual metal deposits on the Si owing to the reaction process. The J – E characteristics of the alkylated surface were also much more stable than those of the H-terminated surface, and the electrochemical properties of such electrodes decayed only very slowly during the passage of anodic photocurrent at this photocurrent density (Figure 2b).

Figure 3 depicts the dependence of the J – E characteristics on the chain length of the alkylating reagent. All of the alkylated Si electrodes showed high open-circuit voltages, indicating that the functionalization step, for any chain length investigated in this work, had not introduced high levels of electrical recombination sites onto the Si surface (Table 1). In fact, the observed photovoltages were very close to the optimal values expected from a junction limited only by minority carrier recombination in the bulk of the semiconductor, as opposed to a device dominated by surface recombination or by capture of majority carriers by the redox ions in the electrolyte.^{22, 24–28}

Figure 3a also indicates that electrodes that had been alkylated with longer chain length reagents showed lower fill factors relative to the fill factor displayed by the methyl-terminated Si surface. Functionalization with $-\text{C}_4\text{H}_9$, for example, produced a unit area series resistance of $\sim 280 \Omega \text{ cm}^2$, as compared to a value of $\sim 17 \Omega \text{ cm}^2$ for a methyl-terminated surface. The larger

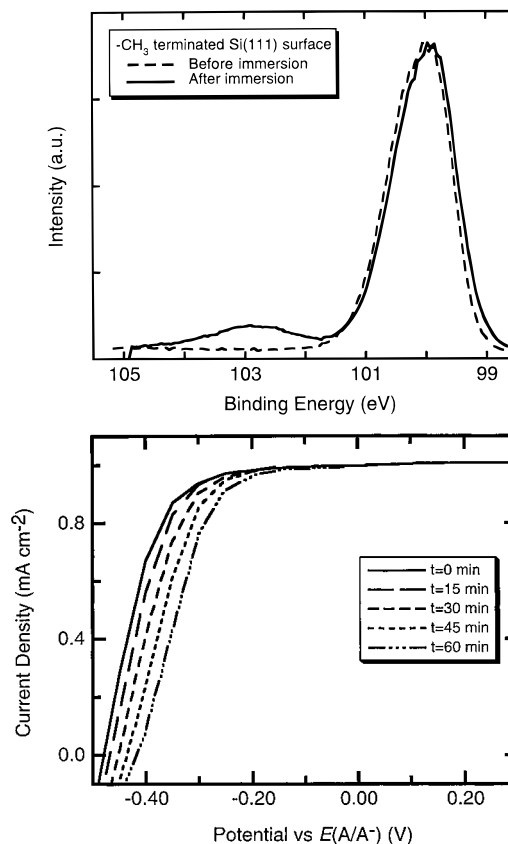


Figure 2. (a) Representative high-resolution XP spectra of the Si 2p region of a $-\text{CH}_3$ -terminated n-type Si(111) surface. The data were collected under conditions similar to those described in Figure 1. The oxide peak occurred 3.0 eV higher than the bulk Si 2p peak, and this surface showed less than one monolayer of oxidized Si. (b) Time-dependence of the J – E behavior of a $-\text{CH}_3$ -terminated surface in contact with $\text{Fe}(\text{CN})_6^{3-/4-}$ (aq) solution.

resistance values clearly degraded the electrochemical performance of the photoelectrode despite a high photovoltage of the system. The increased electrical series resistance displayed by these electrodes is consistent with expectations for an increased charge-transfer resistance through thicker alkyl overlayers that has been observed for self-assembled monolayers of thiols on Au surfaces.²⁹

Figure 3b displays the J – E characteristics of these functionalized electrodes after they had been maintained at a light-limited current density of 1.0 mA cm^{-2} for 60 min. The V_{oc} and fill factor of the $-\text{CH}_3$ - and $-\text{C}_2\text{H}_5$ -terminated surfaces were essentially constant over this illumination period,³⁰ but the fill factors for the $-\text{C}_4\text{H}_9$ - and $-\text{C}_6\text{H}_{13}$ -terminated Si surfaces decayed relatively rapidly under these levels of illumination. In fact, light-limited J – E curves could not be recorded for the $-\text{C}_4\text{H}_9$ - and $-\text{C}_6\text{H}_{13}$ -terminated Si surfaces even at 0.6 V reverse bias after 60 min of illumination in contact with this electrolyte. The data therefore suggest that two competing factors contribute to the initial stability and the subsequent decay of the J – E characteristics of alkyl-terminated Si surfaces in contact with the $\text{Fe}(\text{CN})_6^{3-/4-}$ (aq) solution. The formation of a strong Si–C bond stabilizes the surface and reduces its propensity toward oxidation, whereas the branching ratio between the faradaic current that leads to hole transfer to $\text{Fe}(\text{CN})_6^{4-}$ and that which leads to Si oxidation is sensitive to the packing density, the series resistance, and other structural features of the overlayer. These arguments suggest that shorter alkyl groups will be the most favorable for electrochemical applications because such overlayers have the least series

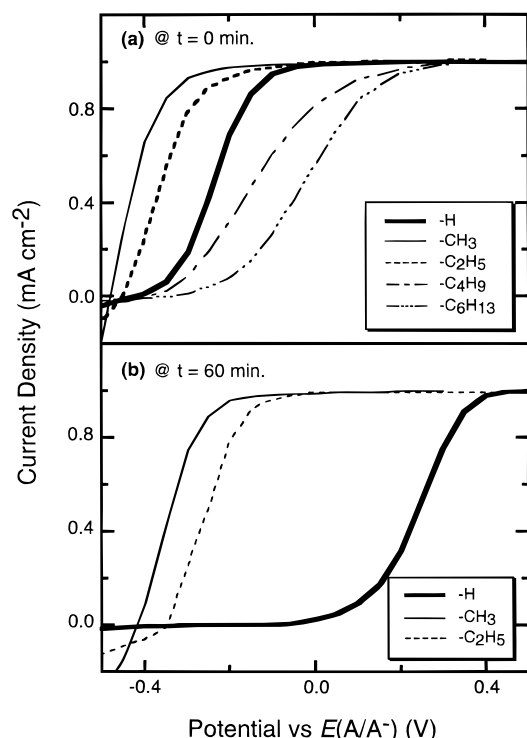


Figure 3. Representative current density–potential (J – E) characteristics of silicon surfaces derivatized with alkyl groups of various chain lengths in contact with 0.35 M $\text{Fe}(\text{CN})_6^{4-}$ –0.05 M $\text{Fe}(\text{CN})_6^{3-}$ (aq). Under illumination, the semiconductor electrode was driven slightly into reverse bias such that the light-limited photocurrent density could be sustained. (a) Immediately after contacting the electrolyte, the $-\text{CH}_3$ - and $-\text{C}_2\text{H}_5$ -terminated surfaces exhibited higher open-circuit voltages (V_{oc}) and higher fill factors than the H-terminated surface, while the $-\text{C}_4\text{H}_9$ - and $-\text{C}_6\text{H}_{13}$ -terminated surfaces exhibited lower V_{oc} values and fill factors than the unalkylated electrodes. (b) After 60 min of illumination at a light-limited photocurrent density of 1.0 mA cm^{-2} , the H-terminated surface showed a very large decrease in V_{oc} and fill factor, whereas the electrodes that had been functionalized with $-\text{CH}_3$ and $-\text{C}_2\text{H}_5$ groups were significantly more stable. The $-\text{C}_4\text{H}_9$ - and $-\text{C}_6\text{H}_{13}$ -terminated surfaces decayed very rapidly under illumination, and light-limited J – E curves could not be recorded even at 0.6 V reverse bias for such surfaces after 60 min of illumination under such conditions.

TABLE 1: Current Density–Potential (J – E) Properties of H-Terminated and Alkyl-Terminated Si(111) Surfaces in Contact with 0.35 M $\text{Fe}(\text{CN})_6^{4-}$ –0.05 M $\text{Fe}(\text{CN})_6^{3-}$ (aq)

terminal group, R	J – E properties in $\text{Fe}(\text{CN})_6^{3-/4-}$ (aq) ^a			
	$t = 0 \text{ min}$		$t = 60 \text{ min}$	
	V_{oc} (V)	fill factor	V_{oc} (V)	fill factor
–H	0.42	0.34	0.22	0.08
–CH ₃	0.48	0.64	0.42	0.57
–C ₂ H ₅	0.45	0.53	0.35	0.46
–C ₄ H ₉	0.40	0.22	<i>b</i>	<i>b</i>
–C ₆ H ₁₃	0.36	0.13	<i>b</i>	<i>b</i>

^a Data were collected at a light intensity sufficient to provide a light-limited photocurrent density of 1.0 mA cm^{-2} . ^b The C_4H_9 - and C_6H_{13} -terminated surfaces decayed rapidly under illumination, and light-limited J – E curves could not be recorded even at 0.6 V reverse bias for such surfaces after 60 min of operation.

resistance to interfacial charge transfer, whereas longer chains might be more suitable for improving the stability of Si in contact with air, where no faradaic current need flow through the circuit. The behavior displayed in Figure 3b also indicates the advantages, in certain applications, that are provided by the two-step chlorination/alkylation procedure, which provides a

facile synthetic route to methylated Si surfaces as well as to surfaces functionalized with longer alkyl chains.

In conclusion, the results described herein demonstrate that the formation of a stable, covalent bond between alkyl chains and silicon surfaces can be used to impart stability to Si photoanodes against oxidation in contact with an aqueous environment. The improved resistance toward oxidation has been achieved without significant compromises to the electrochemical quality of the silicon surface in contact with these electrolytes. The functionalization strategy can be applied in both aqueous and water-containing gaseous ambients and seems to offer a promising approach to modifying, at the molecular level, the chemical properties of Si surfaces for various possible uses in electrochemical and electronic devices.

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References and Notes

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