# Surface Modification of n-Si(111) Electrodes with Brominated and Sulfonylated Alkyl Chains and Their Photoelectrochemical Characteristics

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Bromination of alkenyl-chain-covered n-Si(111) electrodes and their consecutive sulfonylation were demonstrated, and the effects of these functionalization on the photoelectrochemical characteristics were studied in 7.6 M HI + 0.05 M $I_2$ electrolyte under simulated solar illumination.

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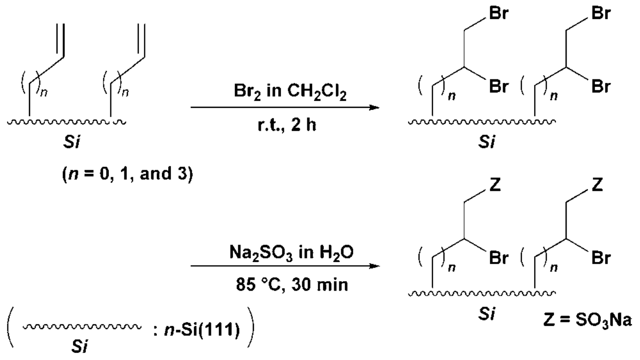
The functionalization of Si surfaces with formation of Si–C bonds has attracted recent interest because of not only stabilizing against surface oxidation in air and/or water but also promising materials as organosilicon hybrid devices.[1–6] We demonstrated that surface methylation in combination with Pt-nanoparticle deposition[7] to n-Si(111) electrodes led to higher open-circuit photovoltages ($V_{OC}$) as well as less degradation in 7.6 M HI/0.05 M $I_2$ under simulated solar illumination than the H-terminated n-Si electrode.[8] Recently, we communicated the modification of the n-Si(111) surface with alkyl chains having the terminal C=C double bond and showed that the $CH_2{=}CH(CH_2)_n$-terminated n-Si(111) electrodes with Pt nanoparticles exhibited higher stability in aqueous electrolytes than n-Si(111) electrodes modified with simple alkyl chains.[9] As a part of our ongoing studies, our effort has focused on the introduction of various functional groups into the surface-modified alkyl chains to improve the efficiency of the semiconductor/electrolyte junction system. The prepared C=C double bond moieties would be a stepping-stone to incorporate different kinds of functionalities, since examples of the direct functionalization on the Si surface were apparently limited.[10] It is anticipated that the introduction of anionic functional groups into the surface of the n-Si(111) electrode might generate much higher $V_{OC}$ since an upper shift of $U_{FB}$ is induced by a change in the potential drop at the formation of Helmholtz double layer. Herein, we report two kinds of modification of the n-Si(111) surfaces through the bromination of terminal C=C bonds of the alkenyl chains and sulfonylation via substitution reaction of the brominated alkyl chains. We further report the photoelectrochemical characteristics of these functionalized electrodes.

Maceration of the n-Si(111) surface with 4-pentenyl groups, n-Si(111)–$(CH_2)_3CH{=}CH_2$,[9] into a solution of $Br_2$ in $CH_2Cl_2$ at ambient temperature for 2 h gave a 4,5-dibromopentyl electrode (Scheme 1).[11] Monitoring the bromination of the electrode by means of XPS analysis, a broadened peak attributable to Br atoms was observed around 66–72 eV (Figure 1). When the immersion time was elongated to 48 h, the Si(111) surface was damaged by oxidation during this bromination stage as evident from the $SiO_2$ signal in the XPS spectrum around 102–104 eV. The same procedure was applied to other $\alpha,\omega$-alkenyl-terminated n-Si(111) surfaces, producing a series of modified electrodes with brominated alkyl chains, n-Si(111)–$(CH_2)_nCHBrCH_2Br$ ($n = 0$, 1, and 3) (Scheme 1).



**Scheme 1.**

The introduced bromine groups could be transferred into other functional groups. Treatment of n-Si(111)–$(CH_2)_3$-$CHBrCH_2Br$ with aqueous $Na_2SO_3$ at 85 °C for 30 min led to the replacement reaction, via an $S_N2$ reaction mechanism, producing n-Si(111)–$(CH_2)_3CHBrCH_2Z$ (Z = $SO_3Na$, Scheme 1). The appearance of the new signal assignable to $SO_3^-$ groups in the XPS S 2p region (166–172 eV)[12] along with the remained Br signal indicated that the replacement reaction was not completed, and most of inner bromide was likely assumed to leave intact probably owing to steric hindrance (Figure 1). Longer immersion into the $Na_2SO_3$ solution advanced the substitution; however, surface oxidation proceeded because the solution was alkaline. Partial substitutions of dibromo-alkylated surfaces with different chain length, n-Si(111)–$(CH_2)_nCHBrCH_2Br$ ($n = 0$, 1, and 3), by sulfonyl groups were conducted in the same manner.

The electrodes with various functional groups and chain lengths were estimated through the measurement of the photoelectrochemical characteristics in 7.6 M HI + 0.05 M $I_2$ under simulated solar illumination (Table 1). Pt nanoparticles were deposited electrochemically on alkyl-modified n-Si(111) surfaces in an aqueous solution of 5 mM $K_2PtCl_6$ and 0.1 M $LiClO_4$ at −1.0 V vs. Ag|AgCl (sat. KCl) with 83 mC·cm$^{-2}$ of electricity passing across the n-Si surface. Figure 2 shows *j–U* curves for the Pt-dotted n-Si(111) electrodes with functionalized $C_3$-alkyl chains.

The $V_{OC}$ values of a series of electrodes covered with both brominated- and sulfonylated-alkyl chains were higher than that of H-terminated n-Si(111) electrode, and hence, the modification of the n-Si(111) with functionalized alkyl groups is, to some extent, effective to generate high $V_{OC}$ and $\eta$. These values, however, were less than those of original alkenyl-terminated one. In particular, modification of the n-Si(111) electrode with brominated-alkyl chain resulted in notable diminution of the photocurrent density. The stabilities of the electrodes were not better than

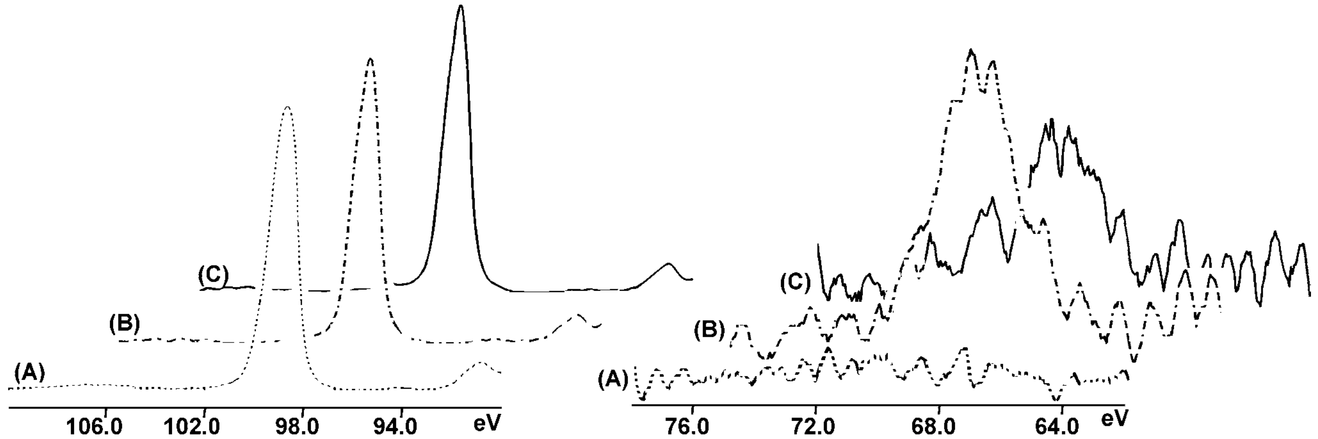


**Figure 1.** XPS spectra in the Si 2p region (left) and Br 3d region (right) of the $CH_2{=}CH(CH_2)_3$-terminated n-Si(111) surface (A; dashed line), the $CH_2BrCHBr(CH_2)_3$-terminated n-Si(111) surface (B; dashed-dotted line), and $CH_2ZCHBr(CH_2)_3$-terminated n-Si(111) surface (C; full line, Z = $SO_3Na$).

**Table 1.** Solar cell parameters for n-Si(111) with alkyls and Pt nanodots[a]

| surface alkyl | $V_{OC}$/V | $j_{SC}$/mA cm$^{-2}$ | FF | $\eta$/% |
|---|---|---|---|---|
| $CH_2{=}CH$– [b] | 0.562 | 13.95 | 0.665 | 5.21 |
| $CH_2{=}CH(CH_2)$– [b] | 0.554 | 15.73 | 0.681 | 5.94 |
| $CH_2{=}CH(CH_2)_3$– [b] | 0.564 | 13.76 | 0.695 | 5.39 |
| $CH_2BrCHBr$– | 0.475 | 11.12 | 0.513 | 2.79 |
| $CH_2BrCHBr(CH_2)$– | 0.490 | 11.80 | 0.591 | 3.42 |
| $CH_2BrCHBr(CH_2)_3$– | 0.439 | 12.86 | 0.533 | 3.16 |
| $CH_2ZCHBr$– [c] | 0.477 | 14.57 | 0.528 | 3.57 |
| $CH_2ZCHBr(CH_2)$– [c] | 0.486 | 14.08 | 0.608 | 4.16 |
| $CH_2ZCHBr(CH_2)_3$– [c] | 0.420 | 13.52 | 0.620 | 3.35 |
| H– [d] | 0.359 | 13.95 | 0.653 | 3.27 |

[a] $j_{SC}$, short-circuit photocurrent density; FF, fill factor; $\eta$, solar energy conversion efficiency. [b] Ref 9. [c] Z = $SO_3Na$. [d] Ref 8c.

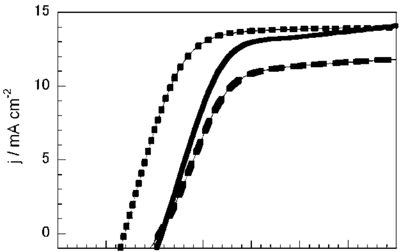


**Figure 2.** Photocurrent density ($j$) vs. potential ($U$) for the $CH_2{=}CH(CH_2)$-terminated and Pt-dotted (dotted line), the $CH_2BrCHBr(CH_2)$-terminated and Pt-dotted (dashed line), and $CH_2ZCHBr(CH_2)$-terminated and Pt-dotted (full line, Z = $SO_3Na$) n-Si(111) electrodes in 7.6 M HI + 0.05 M $I_2$ under simulated solar illumination (AM 1.5 G, 100 mW cm$^{-2}$).

the originals: similar decays to those of the $C_nH_{2n+1}$-terminated n-Si electrodes were observed during the 24 h illumination.[8c] These phenomena were observed in all electrodes with different chain length. It is certain that the function groups introduced at the terminal of the alkyl chain could affect the performance of the solar cell.

In summary, we have demonstrated bromination and sulfonylation of the $CH_2{=}CH(CH_2)_n$– chains on the n-Si(111) surfaces and shown that these modifications had an effect on the performance of the electrode measured in the HI/$I_2$ electrolyte. We are studying the effect of other functional groups on the surface-modified alkyl chains, together with a mechanism for it.

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