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Modification of the *n*-Si(111) Surface with Alkyl Chains Having the Terminal C=C Double Bond

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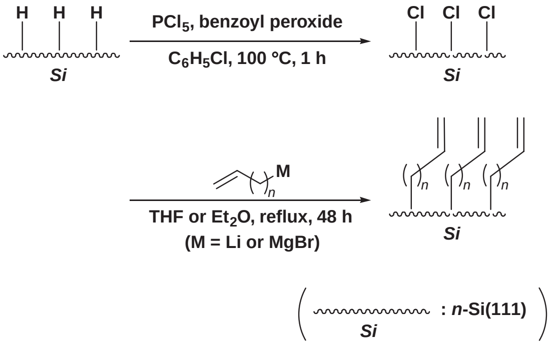
We synthesized a series of the *n*-Si(111) electrodes covered with alkyl chains having the terminal C=C double bond, and found that they gave high V_{OC} as well as high stability in the electrolyte when electrodeposited with Pt nanoparticles, whose size was able to be controlled by the chain length of the alkyl group.

In the last decades, much attention has been paid to thin-film solar cells using inexpensive semiconductor materials such as amorphous Si, polycrystalline Si, and particulate TiO_2 with a photosensitizing dye.[1] Solar to chemical conversion by use of a semiconductor/electrolyte junction has an advantage of lower cost since it does not need to use expensive transparent conductive oxide (TCO) films. In previous work, we have demonstrated that *n*-Si(111) electrodes loaded with Pt nanoparticles generated high open-circuit photovoltages (V_{OC}) of 0.62–0.64 V in 8.6 M HBr/0.05 M Br_2.[2] Although these values were considerably higher than those of conventional solid-state p–n junction Si solar cells, owing to a unique effect of metal nanocontact, the *n*-Si surface showed marked degradation within 1 h due to the gradual surface oxidation in an aqueous electrolyte under illumination.

Chemical modification of the Si surface has recently attracted much interest in view of not only creating functionalities on the surface but also improving the stability of the surface, especially against the surface oxidation in air and in aqueous redox electrolytes.[3–10] We have found that the methylated *n*-Si(111) electrode when dotted with Pt particles exhibited higher V_{OC} than the H-terminated *n*-Si electrode and scarcely showed degradation for more than 24 h, as judged from the measurement of the photocurrent density (*j*) vs. potential (*U*) in 7.6 M HI/0.05 M I_2 under simulated solar illumination.[11] These finding prompted us to investigate how to control the interfacial interaction of Pt nanoparticles with the surface of the *n*-Si(111) electrode. We recently reported the introduction of longer alkyl groups on the Si surface and examined how the chain length affected on the performance of the electrode deposited with Pt particles.[11c] Herein, we report the modification of the *n*-Si(111) surface with alkyl chains having the terminal C=C double bond. Interestingly, 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, owing to the substituent effect of the terminal C=C double bond moiety.

Treatment of the atomically flat H-terminated *n*-Si(111), which is obtained by HF- and NH_4F-etching, with PCl_5 and a catalytic amount of benzoyl peroxide as a radical initiator in C_6H_5Cl at 100 °C for 1 h afforded Cl-terminated *n*-Si(111).[4a,4b] Its maceration in a THF or Et_2O solution of $CH_2{=}CH–(CH_2)_nM$ ($n = 0$–3, M = Li and MgBr) at a reflux temperature for 48 h gave a series of alkylated electrodes (Scheme 1). In this alkylation stage, we found no oxidative damage on the Si(111) surface as confirmed by XPS analysis, which displayed no peak at 102–104 eV attributable to SiO_2. The surface coverage for $CH_2{=}CH–$ and $CH_2{=}CH(CH_2)_3–$ groups was roughly estimated to be 0.62 and 0.46, respectively, by means of the method reported by Chidsey et al.[5d] Although theoretical and experimental studies have revealed that the optimal coverage for the alkylated Si(111) surface is almost 0.5,[5b,5c,7e] the value for $CH_2{=}CH$-terminated *n*-Si(111) surface was somewhat higher, probably owing to organic contaminations on the Si surface.



Scheme 1.

The chain length of the alkyl group on the *n*-Si electrode was found to control the size of Pt nanoparticles, which 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 10 mC·cm^{-2} of electricity passing across the *n*-Si surface. SEM images of the $CH_2{=}CH(CH_2)_n$-terminated *n*-Si(111) surfaces just after Pt electrodeposition exhibited that Pt particles adhered sparsely to all over the *n*-Si(111) surface (Figure 1). The average size of deposited Pt particles and their distribution density were clearly different from those on the H-terminated *n*-Si(111) electrode.[11a] In addition, the average diameter of Pt particles deposited on the $CH_2{=}CH(CH_2)_3$-terminated *n*-Si electrode was larger, and the

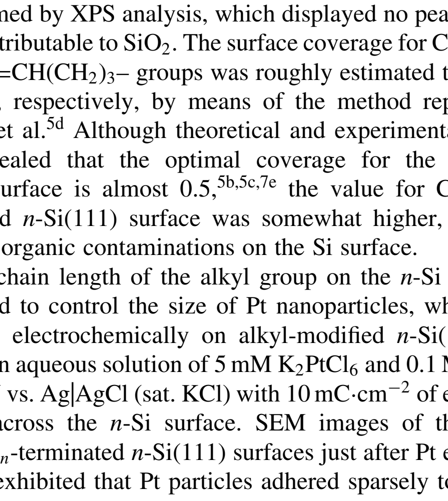


Figure 1. SEM images of the $CH_2{=}CH$-terminated and Pt-dotted *n*-Si(111) (left) and the $CH_2{=}CH(CH_2)_3$-terminated and Pt-dotted *n*-Si(111) surfaces (right).

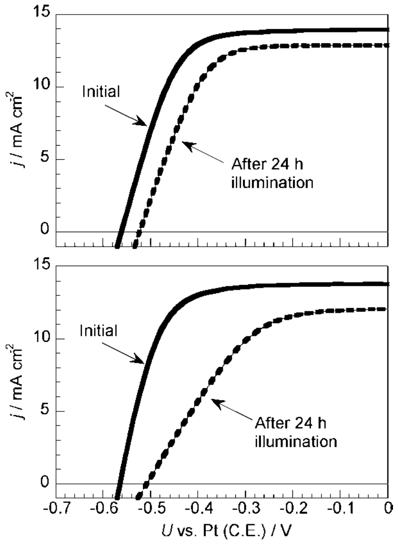


Figure 2. Photocurrent density (j) vs. potential (U) for the $CH_2{=}CH$-terminated and Pt-dotted (top) and the $CH_2{=}CH(CH_2)_3$-terminated and Pt-dotted n-Si(111) electrodes (below) in 7.6 M HI + 0.05 M I_2 under simulated solar illumination (AM 1.5 G, 100 mW cm^{-2}).

distribution density was lower compared with those of the $CH_2{=}CH$-terminated surface, indicating that the electrodeposition of platinum occurred in the bare (non-alkylated) n-Si surface. With elongation of the alkyl chain, the area of the bare n-Si(111) electrode decreased, leading to a fewer number of Pt nanoparticles and larger average size under the identical passing electricity. These observations were consistent with those found for alkylated n-Si(111).[11c]

Figure 2 shows j–U curves for the $CH_2{=}CH$-terminated and the $CH_2{=}CH(CH_2)_3$-terminated n-Si(111) electrodes dotted with Pt particles, respectively. Solar cell parameters are also summarized in Table 1. Although conversion efficiencies (η) fell well short of the value of the methylated electrode, the modification of the n-Si(111) with alkenyl groups is also effective to generate higher V_{OC} and η than those of H-terminated n-Si(111). Furthermore, in contrast with the C_nH_{2n+1}-terminated n-Si electrodes ($n = 4$ and 6), for which the η and the FF values showed obvious decays during the 24 h illumination,[12] such a decay was suppressed to some extent by modifying with alkenyl groups. This inhibiting effect resulted from the terminal C=C double bond moiety, which was most likely to disturb the peeling off the deposited Pt nanodots during the long-term illumination.

In summary, we have synthesized a series of the n-Si(111) surfaces modified with $CH_2{=}CH(CH_2)_n$- chains and demonstrated that the chain length was able to control the size of Pt nanoparticles deposited electrochemically. We have also shown that introduction of $CH_2{=}CH$- moiety into the terminal of the surface-modified alkyl chains is effective to gain high V_{OC} as well as high stability in the electrolyte. Further studies will focus on the introduction of various functional groups into the surface-modified alkyl chains.

Table 1. Solar cell parameters for modified n-Si(111) with Pt nanodots

Surface Alkyl	V_{OC}/V	j_{SC}/mA cm^{-2}	FF	η/%	Ref
$CH_2{=}CH$–	0.562	13.95	0.665	5.21	
$CH_2{=}CH(CH_2)$–	0.554	15.73	0.681	5.94	
$CH_2{=}CH(CH_2)_2$–	0.518	14.32	0.679	5.04	
$CH_2{=}CH(CH_2)_3$–	0.564	13.76	0.695	5.39	
H–	0.359	13.95	0.653	3.27	11c
CH_3–	0.576	14.03	0.702	7.02	11c

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12 The j–U curves for methyl- and alkyl-terminated n-Si(111) electrodes were shown in Ref. 11c.

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