

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

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Solar to chemical conversion has the advantage over thin-film solar cells, to which much attention has been paid owing to use of inexpensive semiconductor materials such as amorphous silicon, because it is unnecessary to use expensive TCO films. We have, thus far, demonstrated that n-Si(111) electrodes loaded with Pt nano-particles generated very high open-circuit photovoltages (V_{OC}) of 0.62-0.64 V in 8.6 M HBr / 0.05 M Br₂.¹ This value was considerably higher than those of conventional solid-state p-n junction Si-solar cells of a similar simple structure, owing to a unique effect of metal nano-contact. However, the n-Si surface showed degradation within 1 hour due to gradual surface oxidation in an aqueous electrolyte under illumination.

Recently, chemical modification of Si surfaces has attracted much interest in view of not only creating functionalities but also improving surface stability,² especially against the surface oxidation in air and in aqueous redox electrolytes. We, therefore, studied the effect of the methylation of the n-Si(111) electrode on both the performance and the stability through measurements of the photocurrent density vs. potential in 7.6 M HI / 0.05M I₂ under simulated solar illumination.³ We found that the modification of the Si surface with methyl groups generated higher open-circuit photovoltages than the H-terminated and Pt-dotted n-Si electrode and enhanced the stability of it. However, the interaction between Pt nano-particles and the electrode surface, in which an alkyl monolayer usually acts as an insulating layer, is not clear. Additionally, a few attempts to investigate methodically the influence of the length of the alkyl chain on the electrode property have been reported thus far.⁴ Herein we report the synthesis of the n-Si(111) surface with alkyl chains having the terminal C=C double bonds and investigate the effect of the chain length on the property of the Pt-dotted electrode.

Modification of the Si surface was, in this work, performed according to published procedures.⁵ Namely, treatment of the H-terminated n-Si(111) wafers with PCl₅ along with a catalytic amount of benzoyl peroxide in C₆H₅Cl, followed by reaction with CH₂=CH(CH₂)_nM (M = Li and MgBr) in THF or Et₂O, gave a series of alkylated electrodes (Scheme 1).

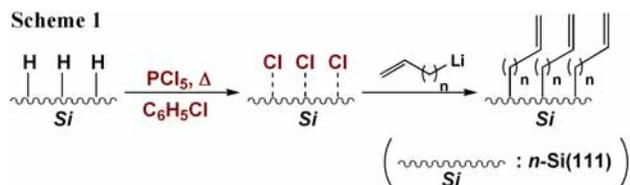


Figure 1 shows SEM images of (A) the CH₂=CH-terminated and Pt-dotted n-Si(111) and (B) the CH₂=CH(CH₂)₃-terminated and Pt-dotted n-Si(111) surfaces just after Pt deposition. Pt nano-particles were deposited electrochemically on each modified n-Si(111) surface in an aqueous solution of 5 mM K₂PtCl₆ and 0.1 M LiClO₄ at -1.0 V vs. Ag|AgCl (sat. KCl) with 10 mC cm⁻² of electricity passing across the n-Si(111) surface, and the size of the Pt particles for the

CH₂=CH(CH₂)₃-terminated and Pt-dotted n-Si was much larger, and their density was much less, than the corresponding values for the CH₂=CH-terminated and Pt-dotted n-Si. The current density vs. potential for electrodeposition of Pt on each modified n-Si surface was similar to that on the H-terminated n-Si, though values of peak potential were somewhat shifted (Figure 2). It strongly indicates that Pt particles were in direct contact with the n-Si surfaces; in other words, they were not deposited on the alkylated parts of the electrode.

Figure 3 shows photocurrent density (j) vs. potential (U) curves for the CH₂=CH-terminated and Pt-dotted n-Si(111) electrode. The value of V_{oc} is almost equal to that for the methylated and Pt-dotted n-Si(111) electrode,⁵ and much higher than that for the Pt-dotted and H-terminated n-Si(111) (c.a. 0.30 V).

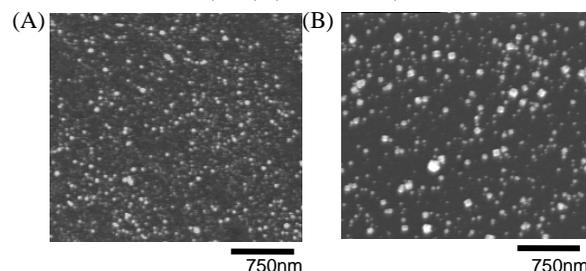


Figure 1. SEM images of (A) the CH₂=CH-terminated and Pt-dotted n-Si(111) and (B) the CH₂=CH(CH₂)₃-terminated and Pt-dotted n-Si(111) surfaces.

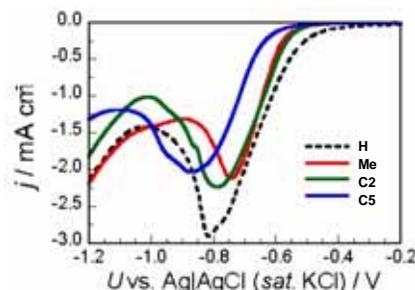


Figure 2. The current density vs. potential for electrodeposition of Pt on H-terminated and alkylated n-Si surfaces.

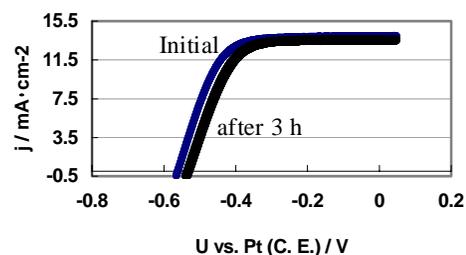


Figure 3. j - U curves for the CH₂=CH-terminated and Pt-dotted n-Si(111) electrode in 7.6 M HI / 0.05M I₂ under the simulated solar illumination (AM 1.5G, 100 mW cm⁻²).

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