

Stabilization of n-Si Electrodes by Surface Alkylation for Use in Efficient and Low-Cost Water Splitting by Solar Light

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The efficient water splitting by solar (visible) light is the most important target in the field of semiconductor photoelectrochemistry. A large number of studies have been made since the pioneering work by Honda and Fujishima (1), but the solar energy conversion efficiency has still remained quite low (< about 1%), except for the work with MOCVD-made high-quality multi-layer semiconductor electrodes such as AlGaAs/Si (2) and GaInP₂/GaAs (3), which are unfortunately inevitably very expensive.

Polycrystalline Si thin films have attracted much attention as one of the most promising materials for low-cost solar energy conversion. We reported before (4-6) that n-Si electrodes with metal nano-dots generated very high open-circuit photovoltages (V_{oc}) of 0.62-0.64 V, higher than those of the conventional p-n Si solid solar cells of a similar simple structure. The finding was of much interest, but had a problem in that the electrodes did not have enough stability for long-term operation. In the present paper, we will report that alkylation of Si surface, as well as coating with metal nano-dots, can overcome this difficulty.

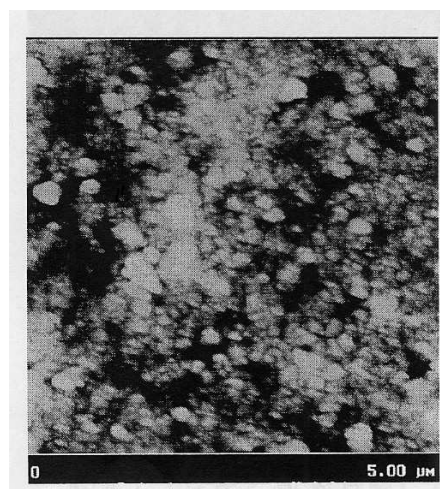
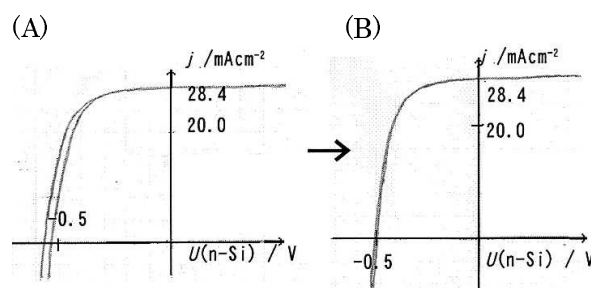
We tried several methods for the alkylation of Si surfaces (7,8). Figure 1 shows photocurrent density (j) vs. potential (U) for a Pt-dotted and surface-methylated n-Si (111) electrode in 8.6 M HBr + 0.05 M Br₂. The methylation was obtained by the method of Lewis et al. (7). Namely, HF- and NH₄F-etched and hence H-terminated n-Si (111) was refluxed in a chlorobenzene solution of PCl₅ under UV illumination, followed by reflux in an ether solution of CH₃MgBr (Grignard reagent). Pt nano-particles were deposited on the methylated Si surface by dropping a colloidal Pt solution prepared by the Bredig method. The j - U curve remained unchanged for 3 h, except for a slight decrease in V_{oc} . On the other hand, the j - U curve for an H-terminated n-Si (111) electrode without the methylation decayed severely in 15 min. The relatively low V_{oc} observed (Figure 1) is likely to be due to the aggregation of Pt nano-particles, as seen in Figure 2, which leads to a decrease in the barrier height for the n-Si/solution contact, according to our theoretical model (4,5).

The methylation of the n-Si surface could be seen easily by an increase in the hydrophobicity of the surface when a water droplet was put on it. XPS analysis also confirmed the methylation of the Si surface, though the surface coverage was difficult to be determined.

The stabilization of n-Si by surface alkylation (methylation) can be explained to be due to the formation of a hydrophobic thin layer on the Si surface, which will prevent the approach or contact of water molecules to the Si surface. The stabilized n-Si electrodes can be used for efficient water splitting by solar light, in combination with other semiconductor electrodes such as N-doped (and hence visible-light absorbing) TiO₂.

Figure 1 Photocurrent density (j) vs. potential (U) for a Pt-dotted and surface-methylated n-Si (111) electrode in 8.6 M HBr + 0.05 M Br₂. (A): A curve at the start of illumination, and (B) that after the continuous 3-h illumination.

Fig. 2 Scanning electron micrograph of the surface of a surface-methylated and Pt-deposited n-Si (111) electrode.



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