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 multiplayer semiconductor electrodes such as AlGaAs/Si (2) and $GaInP_2$/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-tern 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 Br_2. The methylation was obtained by the method of Lewis et al. (7). Namely, HF- and NH_4F-etched and hence H-terminated n-Si (111) was refluxed in a chlorobenzene solution of PCl_5 under UV illumination, followed by reflux in an ether solution of CH_3MgBr (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) TiO_2.

REFERENCES

1) A. Fujishima, K. Honda, *Nature*, **238,** 37 (1972).
2) S. Licht, B. Wang, *Appl. Phys. Lett*., **74**, 4055 (1999).
3) O. Khaselev, J. A. Turner, *Science*, **280**, 425 (1998).
4) Y. Nakato, K. Ueda, H. Yano and H. Tsubomura, *J. Phys. Chem*., **92**, 2316 (1988).
5) Y. Nakato and H. Tsubomura, *Electrochim. Acta*, **37**, 897 (1992).
6) J. Jia, M. Fujitani, S. Yae, Y. Nakato: *Electrochim. Acta*, **42**, 431-437 (1997).
7) A. Bansal, N. S. Lewis, *J. Phys. Chem. B*, **102**, 1067, 4058 (1998).
8) J. Cheng, D. B. Robinson, R. L. Cieero, T. Eberspacher, C. J. Barrelet, C. E. D. Chidsey, *J. Phys. Chem. B*, **105**, 10900 (2001).

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 Br_2. (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.