CHEMISTRY LETTERS, pp. 987-990, 1986.

STRIKINGLY HIGH PHOTOVOLTAGES OF PHOTOELECTROCHEMICAL SOLAR CELLS EQUIPPED WITH PLATINUM-COATED AND ALKALI-ETCHED n-Si ELECTRODES

Yoshihiro NAKATO, Hiroyuki YANO, and Hiroshi TSUBOMURA
Laboratory for Chemical Conversion of Solar Energy
and Department of Chemistry, Faculty of Engineering Science,
Osaka University, Toyonaka, Osaka 560

Open-circuit photovoltages (V_{oc}) of photoelectrochemical cells having an n-Si electrode coated with vacuum-evaporated platinum in an aqueous redox solution have been remarkably increased by etching the Pt-coated n-Si electrode in alkaline solutions. The maximum V_{oc} obtained was 0.685 V, about 15% higher than that of normal p-n junction Si solar cells (0.59 V), demonstrating the possibility of using these cells as highly efficient solar energy converter. The large increase in V_{oc} is explained by a theory recently proposed by us on semiconductor electrodes coated with microscopically discontinuous metal layers.

Photoelectrochemical (PEC) solar cells based on semiconductor-solution junctions have a merit in that a high efficiency can be achieved by use of low-cost semiconductor materials such as polycrystalline films and materials without p-n junctions. This method has another merit in that solar energy can be converted directly into storable chemical energy. The main difficulty for a PEC cell lies in the chemical instability of semiconductor electrodes in aqueous electrolyte solutions. We reported before that thin metal coating not only protects the semiconductor electrodes from corrosion1,2) but also catalyzes the photoelectrode reactions such as hydrogen photoevolution.3,4) This method has a problem, however, in that the coating with a continuous metal layer over a semiconductor electrode results in a small photovoltage which is fixed by the metal-semiconductor junction.1)

Recently we have proposed a theory5) on the mechanism of generation of photovoltages at metal-coated semiconductor electrodes in solution, and concluded that various photovoltaic effects can arise from the structure of the deposited metal layer, quite contrary to the expectation from the conventional potential barrier model for metal-semiconductor contacts.6) An important prediction from this theory is that the photovoltage at a metal-coated n-type semiconductor electrode in a redox solution should be increased by changing the redox potential of the redox couple toward the positive, approaching near the equivalent of the band gap, in cases where the metal layer consists of minute islands, say, 5 nm wide, separated by about 20 nm from each other (Case 3 of Ref. 5). This

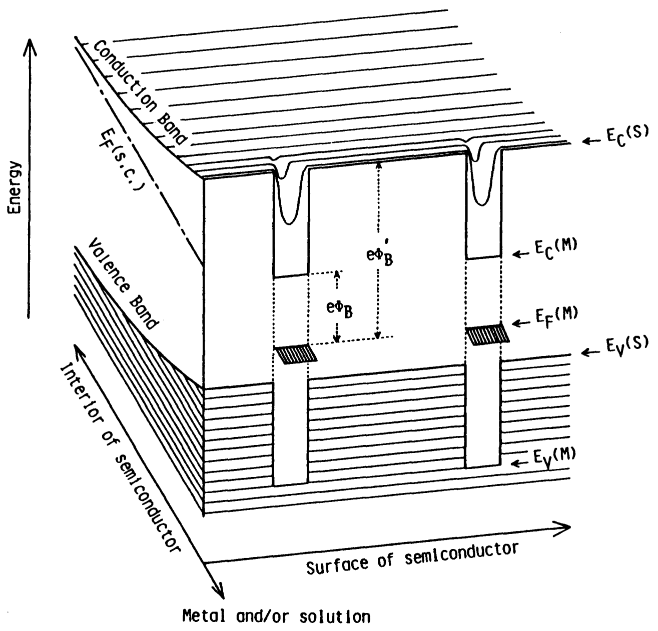

Fig. 1. Schematic energy band diagram for an n-type semiconductor electrode loaded with minute metal islands under illumination in a redox solution. E_F(s.c.): Fermi level of semiconductor, E_F(M): that of metal, E_C(M) and E_V(M): the conduction and valence band edges at the surface respectively in metal-covered areas, E_C(S) and E_V(S): those in metal-free areas.

photovoltaic effect can be explained by an energy band diagram schematically illustrated in Fig. 1. The key point is that the modulation of the band energies at the surface, caused by the presence of metal islands, rapidly decreases toward the interior of the semiconductor in cases where the areas of metal islands are very small, and therefore the effective barrier height at the metal-semiconductor contact becomes $e\Phi_B'$,[5] much higher than $e\Phi_B$ that is derived by the usual concept. A similar conclusion can be derived for p-type semiconductors.

The above-mentioned theoretical prediction implies that a microscopically discontinuous metal layer on a semiconductor electrode does not spoil the photovoltage arising from a semiconductor-solution junction, and yet retains the same catalytic function and even the same stabilizing function as that of a continuous metal layer in cases where naked parts of the semiconductor surface are passivated, thus showing a new important approach to stable and highly efficient solar cells. In the present letter we will report on remarkably increased photovoltages observed at platinum-coated and alkali-etched n-Si electrodes, which can be explained well by the above-mentioned model of Fig. 1.

The n-Si electrodes were prepared from single crystal n-Si wafers having a resistivity of 0.4 to 0.8 Ωcm and cut perpendicular to the <111> axis. After the electrodes were washed in acetone and etched in a 10% HF solution, platinum was evaporated under an argon atmosphere of 0.13 Pa by use of the electron-beam evaporation method. The thickness of deposited Pt was 3 nm, as monitored with a quartz oscillator. The photocurrent (j)-potential(E) curves were studied for PEC cells each consisting of a Pt-coated n-Si electrode, a Pt-plate counterelectrode, and an aqueous redox solution.

The dashed line in Fig. 2 shows a j-E curve for an n-Si electrode coated with a 3-nm Pt layer in a 8.6 M HBr/0.1 M Br_2 solution (M = mol/dm^3). The open-circuit photovoltage (V_{oc}) is only 0.28 V.[1] Interestingly, the j-E curve was strikingly improved by immersing the electrode in a 4 M NaOH solution at 90 °C for 3 min and

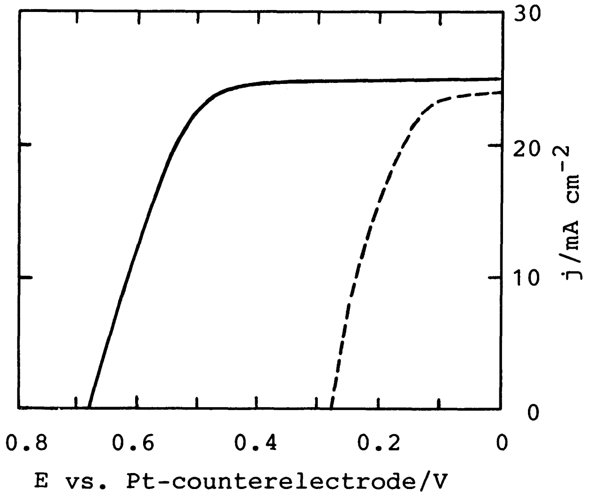

Fig. 2. Photocurrent (j)-potential ( ) curves for Pt-coated n-Si (---) and Pt-coated and alkali-etched n-Si (——) in a 8.6 M HBr/0.1 M Br_2 solution under simulated solar AM 1 (100 mW/cm^2) irradiation.

then in a 0.25 M NaOH solution containing 0.6 M 2-propanol at 90 °C for 3 min. The best j-E curve so far obtained is shown by the solid line in Fig. 2, yielding a V_{oc} of 0.685 V, a short-circuit current (j_{sc}) of 25.0 mA/cm^2, a fill factor (FF) of 0.666, and a conversion efficiency of 11.4% under simulated solar AM 1 (100 mW/cm^2) irradiation. The Pt-coated and alkali-etched n-Si electrodes were stable in contrast to naked n-Si electrodes which degrade rapidly.

It should be emphasized that the V_{oc} for Pt-coated and alkali-etched n-Si is very high, about 15% higher than that of normal solid state p-n junction Si solar cells (≈0.59 V). This indicates that highly efficient solar cells can be obtained from electrodes of the present type if j_{sc} and FF are increased by using, for instance, an n-Si electrode with a matte-textured surface and by optimizing various cell parameters such as the distance between the two electrodes, the solution composition, etc.

Scanning electron microscopic investigations showed that the Pt layer evaporated on n-Si looked quite continuous under a resolution of about 8 nm,5) and that, after the alkali etching, partial peeling off 1-5 μm in breadth was observed. This peeling off seems to indicate that the evaporated Pt layer has very small holes or gaps, through which the alkaline solution penetrates and dissolves the underlying n-Si crystal. It is likely therefore that partial dissolution of the underlying Si occurs even in those parts where the Pt layer remains, and makes the Pt-Si contact discontinuous as schematically shown in Fig. 3. Based on such a discontinuous structure of the Pt-Si contact, the generation of the above-mentioned high V_{oc} can be explained by our afore-mentioned model of Fig. 1.

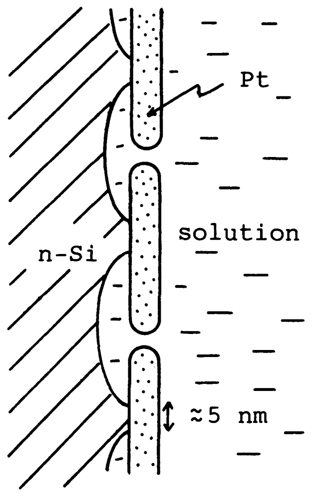

Fig. 3. Expected cross section of a Pt-coated and alkali-etched n-Si electrode near the surface.

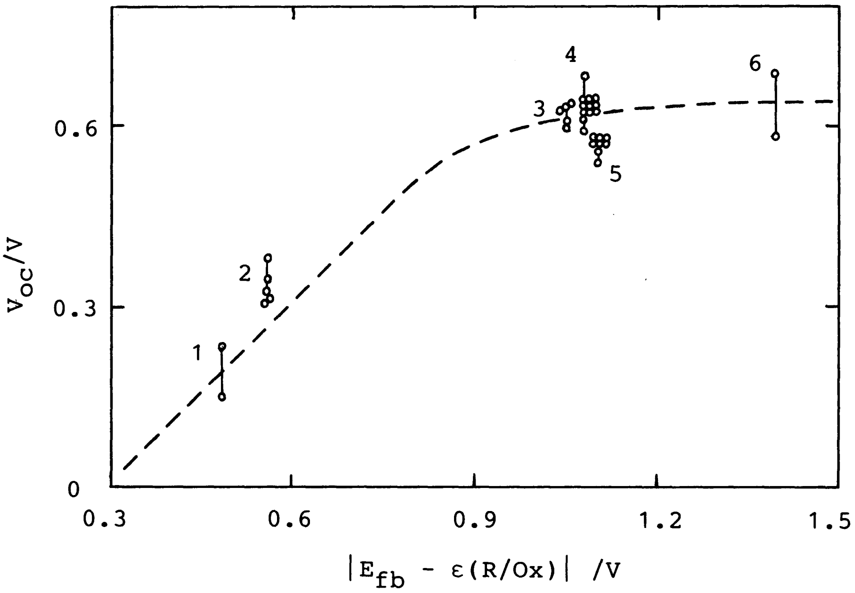

Fig. 4. Plots of V_{oc} vs. $|E_{fb} - \varepsilon(R/Ox)|$. Redox coupes used are 1 $[Fe(C_2O_4)_3]^{4-}/[Fe(C_2O_4)_3]^{3-}$(pH 6.2), 2 I^-/I_3^- (7.6 M H^+), 3 Fe^{2+}/Fe^{3+}(pH 0.5), 4 Br^-/Br_2(8.6 M H^+), 5 $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$(pH 7.6), 6 Br^-/Br_2(pH 2.9).

In Fig. 4, the V_{oc} is plotted against the difference between the redox potential ε(R/Ox) of a redox couple in solution and the flat band potential E_{fb} of naked n-Si determined from the onset potential of the anodic photocurrent in a redox-free electrolyte solution. It is seen that V_{oc} increases linearly with increasing $|\varepsilon(R/Ox) - E_{fb}|$ and then becomes constant. This behavior is just the one expected from our theoretical model of Fig. 1 and supports it. The Pt-coated n-Si electrodes without alkali etching showed constant low V_{oc} (cf. the dashed line in Fig. 2), irrespective of ε(R/Ox).

In conclusion, the present work has revealed that a high V_{oc}, exceeding that of normal p-n junction Si solar cells, can be obtained by using a PEC cell having a Pt coated n-Si electrode. The result supports our model proposed for metal coated semiconductor electrodes and opens up a new approach to stable and highly efficient solar cells.

References

1) Y. Nakato, T. Ohnishi, and H. Tsubomura, Chem. Lett., 1975, 883.

2) Y. Nakato, K. Abe, and H. Tsubomura, Ber. Bunsenges. Phys. Chem., 80, 1002 (1976).

3) Y. Nakato, S. Tonomura, and H. Tsubomura, Ber. Bunsenges. Phys. Chem., 80, 1289 (1976).

4) Y. Nakato, M. Shioji, and H. Tsubomura, Chem. Phys. Lett., 90, 453 (1982).

5) Y. Nakato and H. Tsubomura, J. Photochem., 29, 257 (1985).

6) S. M. Sze, "Physics of Semiconductor Devices," 2nd ed, John Wiley & Sons, Inc., N.Y. (1981).

(Received April 2, 1986)