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EFFICIENT PHOTOELECTROCHEMICAL CONVERSION OF SOLAR ENERGY WITH n-TYPE SILICON SEMICONDUCTOR ELECTRODES SURFACE-DOPED WITH IIIA-GROUP ELEMENTS

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The stability of an n-type silicon (n-Si) electrode was remarkably improved by the doping in a thin surface layer with boron, aluminium or indium. Photoelectrochemical cells having an n-Si electrode surface-doped with boron and coated with a small amount of platinum or palladium converted light energy into either electricity or chemical energy via decomposition of hydrogen iodide into hydrogen and iodine without external bias with an outstanding high efficiency.

The use of semiconductor photoelectrochemical cells is one of the most promising methods for solar energy conversion. So far attention has been paid mostly to the photovoltaic effect at Schottky barriers formed at semiconductor-solution junctions.$^{1-3)}$ Such junctions indeed give rise to photocurrents at high quantum yields, but the problems are the photocorrosion of semiconductors used and the low output photovoltages resulting from the energetical relaxation of holes or electrons at the surface due to the presence of surface states (e.g., surface-trapped holes$^{4)}$).

We have recently been studying the nature of surface-doped semiconductor electrodes that have p-n or n-p junctions near the surface. In the present letter we will report that an n-type silicon (n-Si) electrode surface-doped with a IIIA-group element such as boron works as a stable and efficient photoanode for solar energy conversion.

The single crystal wafers of n-Si that we used were ∿0.3 mm thick, doped with phosphorus at the concentration of (1 - 2) x 10^{16} cm^{-3}, and cut perpendicular to the (111)-axis. The wafer (∿0.5 cm^2 in area) was polished with alumina powder, and etched in a solution containing hydrofluoric acid, nitric acid, and a small amount of bromine. A saturated methanol solution of boron trioxide (B_2O_3) was put on one face of the wafer, and the wafer was heated at 1000 °C for 2 h in the air. The wafer thus treated was then washed, and etched in hydrofluoric acid for 60 s. Ohmic contact was made on the opposite face with indium-gallium alloy.

Figure 1 shows current-potential (j-U) curves for a non-surface-doped n-Si electrode under illumination in a 57% (or 7.6 M, M ≡ mol/dm^3) hydrogen iodide solution at 20 °C obtained by using platinum as a counter electrode and a Hokutodenko HA 101 potentiostat. The onset potential of the anodic photocurrent was ca. -0.5

V vs. SCE at the first forward sweep of potential, but shifted to the positive direction more and more at each succeeding sweep.

The solid line in Fig. 2 shows a j-U curve for an n-Si electrode surface-doped with boron (B) as described above under illumination in a 57% HI solution. As the photocurrent flowed, the solution near the surface of the n-Si electrode became more and more brown. This shows that the current corresponds to the oxidation of iodide ions into iodine or triiodide ions. Under illumination at wavelengths (λ) longer than 690 nm where the solution was transparent, the j-U curve remained unchanged during the cyclic sweeps of potential for 4 h, except for a slight shift of the onset potential of the photocurrent (∿0.02 V) in the initial period of illumination. Similar results were obtained for n-Si wafers surface-doped with aluminium or indium.

The broken line in Fig. 2 shows a j-U curve for an n-Si electrode surface-doped with B and coated with a thin palladium film of ca. 5 nm thick by the vacuum evaporation method. The photocurrent in the range of -0.6 to 0.0 V vs. SCE is largely enhanced in comparison with the B-doped electrode, suggesting that the deposited Pd acts as an effective mediator for the hole transfer from the electrode into I^- ions in solution. Nearly the same result was obtained with the B-doped-Pt-deposited electrode.

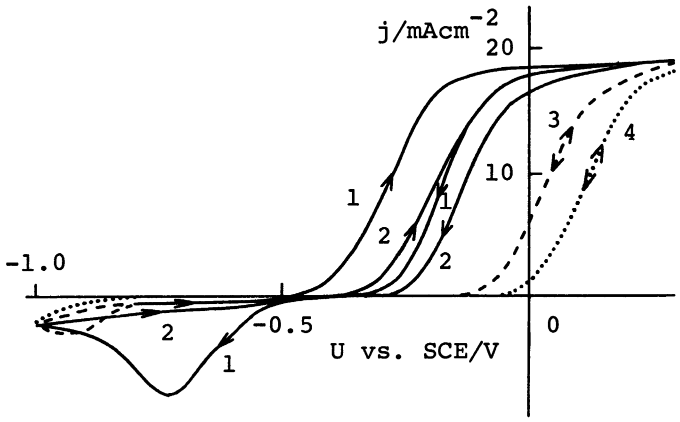

Fig. 1 Current-potential (j-U) curves for a non-surface-doped n-Si electrode under illumination. 1: 1st sweep and 2: 2nd sweep. 3(----) and 4(····) are j-U curves after cyclic sweeps for 30 and 60 min, respectively. The sweep rate is 50 s/V.

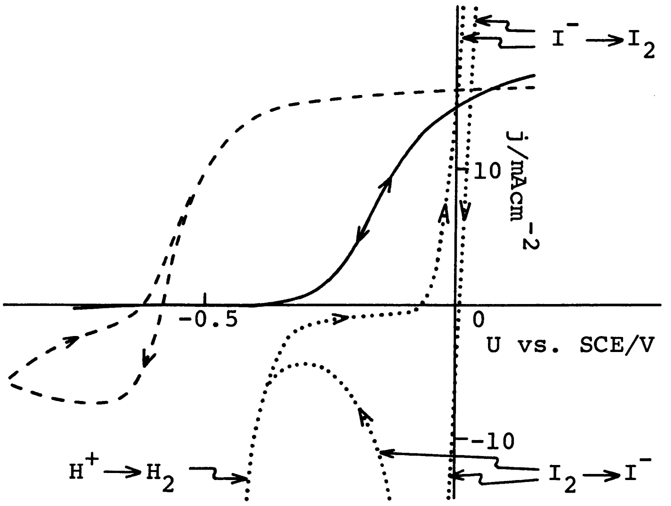

Fig. 2 A current-potential curve for a boron-doped n-Si electrode (——), and that for a boron-doped-palladium-deposited n-Si electrode (----) under illumination in a 57% HI solution. Dotted lines (····) are for a platinum electrode. The sweep rate is 30 s/V.

Figure 3 shows photocurrents vs. time for the B-doped n-Si electrode and the B-doped-Pd-deposited n-Si electrode, in comparison with that for a non-surface-doped n-Si electrode. The currents were measured in a 57% HI solution under illumination at λ > 690 nm with the potential kept at 0.0 V vs. SCE for all the cases.

It is seen that the n-Si electrode is stabilized considerably by doping with B. The stability is further increased by the metal deposition. The decreased currents for the n-Si electrodes were restored to the initial values by dipping the electrodes in a hydrogen fluoride solution. This fact suggests that the decrease in the current is attributable to the formation of a thin oxide layer at the electrode surface.

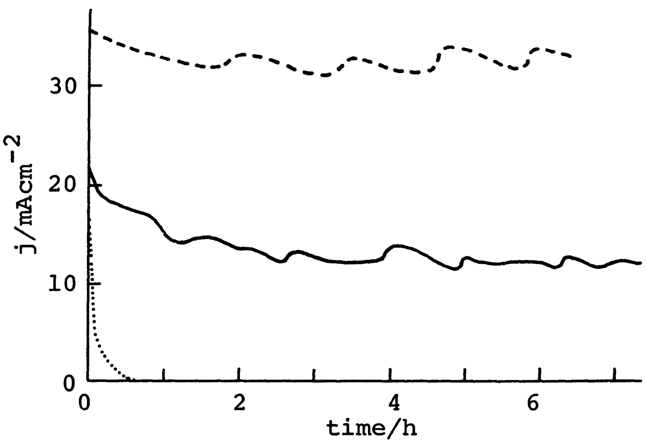

Fig. 3 A photocurrent vs. time curve for a B-doped n-Si electrode (———), that for a B-doped-Pd-deposited n-Si electrode (----), and that for a non-surface-doped n-Si electrode (····).

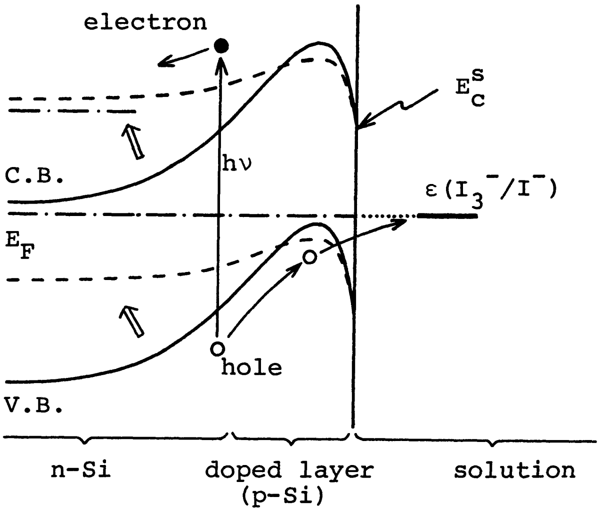

Fig. 4 Schematic energy band model in the equilibrium state (———) and under illumination (----). C.B.: conduction band. V.B.: valence band.

The stabilization of n-Si electrodes by doping with B, Al, or In is tentatively explained by a schematic energy band model shown in Fig. 4. Since the doped surface layer should be of p-type conductivity,[5)] a p-n junction will be formed between the layer and the inner n-Si semiconductor. The conduction band edge at the surface of the Si electrode (E_C^S) in contact with an HI solution is estimated, from the onset potential of photocurrent observed in the first sweep of potential at an etched non-doped n-Si electrode, to lie ca. 0.5 V above the redox potential of an I_3^-/I^- couple, $\varepsilon(I_3^-/I^-)$. Since the bandgap of Si is 1.1 eV, the valence band edge at the surface is ca. 0.6 V lower than $\varepsilon(I_3^-/I^-)$. As the valence band edge in the doped (p-type) layer is very close to the Fermi level (E_F), which coincides with $\varepsilon(I_3^-/I^-)$ in the equilibrium state in the absence of illumination, the downward band bending should be present near the interface between the B-doped layer and the solution (Fig. 4). Such a band bending should push the photogenerated holes a little inward from the surface (or make their density just at the surface quite low) and prevent them from causing corrosive reaction of the electrode. If boron is doped at a high density, the band bending is steep and the surface barrier for holes is thin enough for them to tunnel directly into the electron donors (I^- ions or deposited metal) at the surface. The photovoltage is thought to arise from the p-n junction, as shown in Fig. 4.

In Fig. 2, the dotted lines are current-potential curves for a Pt electrode in an HI solution. It can be seen from Fig. 2 that the B-doped-Pd-deposited n-Si electrode can be used to construct photoelectrochemical cells which effectively convert solar energy into either electric or chemical energy. A cell for the photoelectric conversion, which consisted of the above B-doped-Pd-deposited n-Si electrode, a counter Pt electrode, and a 7.5 M HI solution containing 0.1 M I_2, showed a current-voltage characteristics having the open circuit voltage ∿0.55 V, the short circuit current density ∿29 mA/cm^2, and a fill factor ∿0.57 under illumination at $\lambda > 690$ nm by use of a 500 W Xe-lamp at a power density 42 mW/cm^2, which was determined with an Eppley thermopile. The energy conversion efficiency was calculated to be ∿20%. This is only a preliminary value and will be improved further by optimising various experimental conditions.

A cell for the photochemical conversion was constructed by using the same n-Si and counter electrodes as above and a 7.6 M HI solution, which was separated into anode and cathode compartments with a commercial cation exchange membrane. Under the same illumination conditions as above, the short circuit current of 10 - 16 mA/cm^2 was attained, and the solution near the n-Si electrode became brown and gas evolution was observed at the Pt electrode. This means that HI is decomposed into I_2 (or I_3^-) and H_2. Since the change in the Gibbs energy of this reaction under the present experimental condition is estimated to be ∿80 kJ/mol (or ∿0.4 eV/ion) from the current-potential curves at a Pt electrode (the dotted lines in Fig. 2), the energy conversion efficiency was calculated to be 10 - 15%. This value is, to our knowledge, the highest of the chemical conversion efficiencies without external bias ever reported.6)

We can thus conclude that to dope semiconductors in a surface layer is an excellent method to obtain effective photo-electrodes, or probably photo-catalysts.

References

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6) The short circuit current increased to ∿20 mA/cm^2 when the cation exchange membrane was removed.

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