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Efficient Solar to Chemical Conversion with an n-Type Amorphous Silicon/p-Type Crystalline Silicon Heterojunction Electrode

Keiichi UEDA, Yoshihiro NAKATO,* Hiromi SAKAMOTO, Yuichi SAKAI,
Michio MATSUMURA, and Hiroshi TSUBOMURA*
Laboratory for Chemical Conversion of Solar Energy and Department of Chemistry,
Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560

An n-p heterojunction silicon (Si) electrode was prepared by depositing an n-type amorphous Si layer on a p-type crystalline Si wafer by the plasma CVD method. It worked as an efficient hydrogen evolving photocathode when coated with a thin platinum layer as a catalyst. A photoelectrochemical cell was constructed with an electrode of this type and a platinum counter electrode separated by a cation exchange membrane. It decomposed hydrogen iodide into hydrogen and iodine with the conversion efficiency of 10.8% (AM1, 100 mW/cm^2), the highest of the efficiencies so far reported for the solar-to-chemical conversion without an external bias.

Semiconductor photoelectrochemical (PEC) cells have attracted much attention from the view point of solar energy conversion. By this method, solar energy can be converted directly into storable chemical energy,$^{1-4)}$ and it would be possible to develop a system which competes in efficiency and cost with an indirect method for the chemical conversion by a solid solar cell combined with an electrolyzer.

We reported before$^{3-5)}$ that hydrogen iodide can be decomposed into hydrogen and iodine in a PEC cell equipped with a platinum coated p^+-n or n^+-p junction Si electrode and a platinum counter electrode. The cell was stable and fairly high solar-to-chemical conversion efficiencies of 7.8 to 8.2% were obtained. In these studies the p^+-n or n^+-p Si electrodes were prepared by doping n- or p-type single crystal Si wafers with boron or phosphorus, respectively, by either thermal diffusion or ion implantation method.

For the purpose of increasing the conversion efficiency, we prepared an n-p heterojunction Si electrode by depositing n-type hydrogenated amorphous Si (n-a-Si) on a p-type crystalline Si (p-c-Si) wafer by the plasma CVD method (Fig. 1). This is a new type of PEC electrodes, though work has been done on the photovoltaic effect at the n-a-Si/p-c-Si heterojunction by Hamakawa et al.,$^{6)}$ who used this junction as a part of a tandem-type solid solar cell (ITO/n-i-p a-Si/n-a-Si/p-c-Si/Al) yielding a high solar-to-electric conversion efficiency of 13.3%.

Figure 2 shows a schematic energy band diagram for the platinum coated n-a-Si/p-c-Si heterojunction electrode. It was reported recently$^{7,8)}$ that the discontinuity in the valence band at the a-Si/c-Si heterojunction is less than 0.15 eV, and therefore the discontinuity in the conduction band is calculated to be 0.55 to 0.70 eV from the band-gaps of a-Si (about 1.8 eV) and c-Si (1.1 eV). If we assume that the n-a-Si layer is highly doped, an inversion layer is expected to be formed near the surface of p-c-Si as shown in Fig. 2, leading to the generation of a high photovoltage under illumination. Though there is a large discontinuity in the conduction band as mentioned above, electrons will be able to transfer from the conduction band of p-c-Si to that of n-a-Si and to the Pt layer probably via impurity or defect levels present in the highly doped n-a-Si layer.

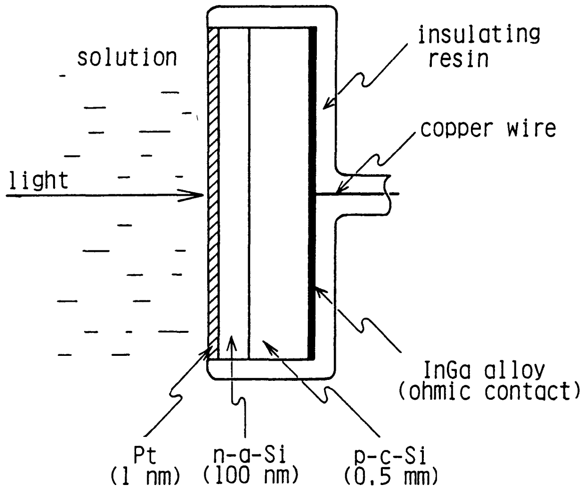

Fig. 1. Schematic cross section of a platinum coated n-a-Si/p-c-Si heterojunction electrode.

From Figs. 1 and 2 we can expect that the n-a-Si/p-c-Si heterojunction electrode has the following advantages over the n^+-p homojunction Si electrode. One arises from the so called "window effect" of the a-Si layer, having a band-gap wider than c-Si which allows a large part of the incident light to pass through the highly doped n-a-Si layer where electron-hole recombination occurs strongly via high-density intra-gap levels[9] and to be absorbed in the underlying p-c-Si layer where photocurrent is generated efficiently. Another arises from the fact that the plasma CVD method employed for the deposition of n-a-Si causes less damage on the p-c-Si wafer surface than the thermal diffusion or the ion implantation method necessary for the cases of the n^+-p homojunction. Accordingly, the recombination rate near the surface of the p-c-Si substrate becomes smaller and we get more photocurrent. The n-a-Si/p-c-Si junction may be advantageous also in view of the cost of preparation.

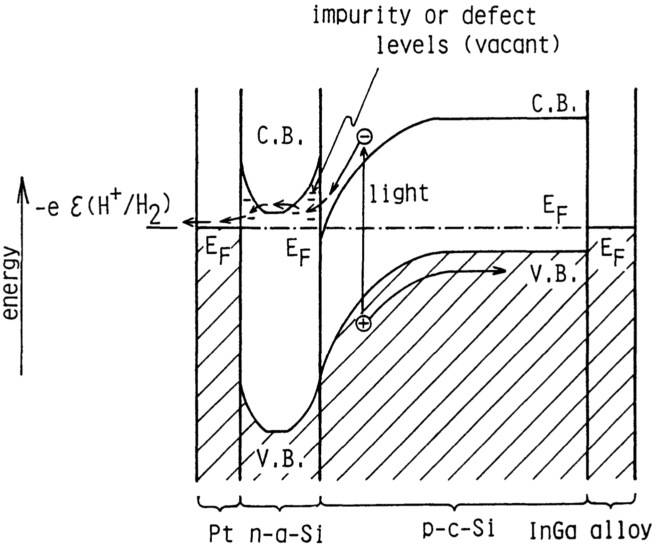

Fig. 2. Schematic energy band diagram for a Pt-coated n-a-Si/p-c-Si heterojunction electrode in an acid solution under equilibrium. C.B.: Conduction band. V.B.: Valence band. E_F: Fermi level. ⊖: Electron. ⊕: Hole. $\varepsilon(H^+/H_2)$: Redox potential for hydrogen evolution.

The platinum coated n-a-Si/p-c-Si heterojunction electrodes (Fig. 1) were prepared as follows: Single crystal p-Si (100) wafers, obtained from Shin-Etsu Handotai Co., were polished, cleaned with acetone, boiled in 61% nitric acid, and then etched in 12% hydrogen fluoride. The wafer thus cleaned was immediately put into a plasma CVD apparatus, and an n-a-Si layer was formed by RF glow discharge of a 0.266 kPa hydrogen-diluted silane (10%) gas containing phosphine at a PH_3/SiH_4 ratio of 0.02. The flow rate of the gas was 50 cm^3/min. The temperature of the p-Si substrate was kept at about 250 °C, and the RF power was 2 W/cm^2. The n-a-Si layer thus deposited contained microcrystallites, as suggested by the X-ray diffraction analysis. Platinum was deposited on the n-a-Si layer by the electron-beam evaporation method under $(2.7-5.4)\times10^{-4}$ Pa.

The dashed line in Fig. 3 shows a photocurrent density (j)-potential (U) curve for a PEC cell, equipped with an n-a-Si (120 nm)/p-c-Si (500 µm) heterojunction electrode, a Pt counter electrode, and a 7.6 M HI/0.05 M I_2 solution ($M = mol/dm^3$), under simulated solar AM1 illumination. The j-U curve was improved by coating the Si electrode with a 1 nm thick platinum layer as a catalyst (solid line), as was observed for the n^+-p homojunction Si electrodes.$^{3)}$

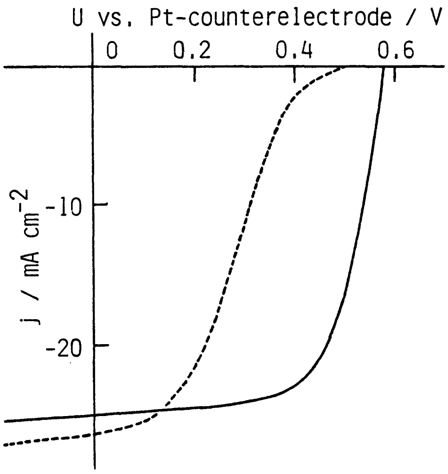

Fig. 3. Current density (j) vs. potential (U) for an n-a-Si/p-c-Si heterojunction electrode (---) and that for a Pt-coated one (——) under illumination in a stirred 7.6 M HI/0.05 M I_2 solution.

Investigations were continued to clarify the effect of the thickness (d) of the n-a-Si layer, the resistivity (ρ) of the p-c-Si wafer, and the presence of a thin silicon oxide layer between n-a-Si and p-c-Si. For the case where p-c-Si of ρ = 2.25 Ω cm was used, the open-circuit photovoltage V_{oc} was small (ca. 0.45 V) if d was less than 50 nm, but it increased with increasing d, reaching 0.57 to 0.58 V for d of 70 nm or more. The latter V_{oc} value is almost the same as that obtained for the n^+-p homojunction Si electrode.$^{3)}$ The short-circuit current density j_{sc} slightly decreased with increasing d owing probably to the light absorption of the n-a-Si layer. With d = 100 nm and ρ of the p-c-Si changed from 0.4 to 2.25 Ω cm, the j_{sc} increased from 19.9 to 26.1 mA/cm^2, while the V_{oc} was nearly constant (0.57-0.58 V). The V_{oc} decreased to 0.54 V when ρ became very high, 16-24 Ω cm. When a silicon oxide layer was interposed between n-a-Si and p-c-Si, by heating p-c-Si at 300 °C in a wet O_2 atmosphere for one hour before the deposition of n-a-Si, the photocurrent was very much suppressed. This is contrary to the case for an n-type indium-tin-oxide/p-type Si heterojunction where the j-U curve was reported to be improved.$^{10)}$ Both the j-U curves in the dark and under illumination showed ohmic behavior when the surface of p-c-Si had been etched by hydrogen plasma before the depositon of n-a-Si for the purpose of removing the thin silicon oxide layer on a chemically etched p-c-Si wafer.

The solar-to-chemical conversion efficiency was investigated using the Pt (1 nm)-coated n-a-Si (100 nm)/p-c-Si (2.25 Ω cm) electrode that gave the best characteristics in the PEC cells of the photovoltaic type mentioned above. The solid line in Fig. 4 shows a hydrogen evolution photocurrent in a 3 M HBr solution under simulated solar AM1 (100 mW/cm^2) illumination. The light-intensity limited current observed below +0.2 V vs. Ag/AgCl is about 33 mA/cm^2, much higher than that observed for the Pt-coated n^+-p homojunction Si electrodes,[3] indicating the "window effect" of the n-a-Si layer mentioned before. The dashed line in Fig. 4 shows the hydrogen evolution current in a platinum electrode. Since the thermodynamic hydrogen evolution potential $\varepsilon(H^+/H_2)$ is nearly equal to the onset potential of this current, the shaded rectangle in Fig. 4 represents the maximum energy saving for the photo-assisted electrolysis, yielding a solar-to-chemical conversion efficiency Φ_{chem} (AM1) of 11.5%.

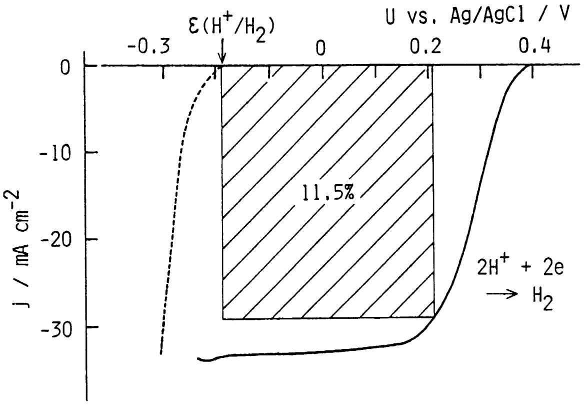

Fig. 4. Hydrogen evolution current density (j) vs. potential (U) for a Pt-coated n-a-Si/p-c-Si heterojunction electrode (——) in a stirred 3 M HBr solution under simulated solar AM1 (100 mW/cm^2) illumination, compared with that for a platinum electrode (---).

The decomposition of HI into H_2 and I_2 was carried out with a PEC cell having the same Si electrode as above in a 3 M HBr solution (catholyte) and a platinized platinum electrode in a 3 M HI/0.01 M I_2 solution (anolyte). Both electrodes were connected together externally and the catholyte and the anolyte were separated by a commercial cation exchange membrane (Asahi Glass Co., Selemion K-101). A photocurrent density of 30.0 mA/cm^2 was obtained under simulated solar AM1 (100 mW/cm^2) irradiation. Since the Gibbs energy change of the HI decomposition in the above solution was determined before to be 0.36 eV/ion (69.5 kJ/mol),[3] the chemical conversion efficiency is calculated to be 10.8%. This value is the highest efficiency reported so far for the solar-to-chemical conversion without an external bias.

In conclusion, the n-a-Si/p-c-Si heterojunction has shown some superiority over the n^+-p homojunction as a hydrogen evolving photocathode. A high conversion efficiency of 10.8% obtained above is encouraging for the direct solar-to-chemical conversion. Further improvement will be made by optimizing the structure of the junction, for which the clarification of remaining questions such as the effect of the conduction band discontinuity and the intervening thin oxide layer at the n-a-Si/p-c-Si interface is necessary.

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