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p-n Junction Silicon Electrode Coated with Noble Metal for Efficient Solar Photoelectrolysis of Hydrogen Iodide

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The photooxidation of iodide ions on n-type silicon electrodes highly doped with boron from the surface in hydrogen iodide or hydrogen iodide/iodine solutions was investigated. Two doping methods were employed: thermal diffusion and ion implantation. The electrode was remarkably stabilized by coating with a 2 to 3 nm-thick platinum layer, followed by heat-treatment at about 400 °C for *ca.* 10 min. The photocurrent was stable for more than 500 h at a density of the order of 10 mA cm^{-2}. The boron-doped and Pt-coated n-Si electrode also generated a photovoltage much higher than that for a Pt-coated n-Si electrode, showing an advantage of forming the p-n junction. Photoelectrochemical cells made of a boron-doped-Pt-coated n-Si electrode, a platinized Pt counter electrode, and a commercial cation exchange membrane were found to photoelectrolyze hydrogen iodide without externally applied voltage into hydrogen and iodine with a solar-to-chemical energy conversion efficiency (ϕ^s_{chem}) under simulated AM 1 solar radiation of 8.2%, probably the highest of the ϕ^s_{chem} values observed for the cells working without external voltage.

The semiconductor photoelectrochemical (PEC) cell is an interesting device for chemical conversion of solar energy. The basic idea of this device is to use the photovoltage generated in the semiconductor directly to drive electrochemical reactions at the semiconductor-solution interface. Extensive work has so far been made on such PEC cells,[1—7] but attention has been paid mostly to the photovoltaic effect at the Schottky junction formed at the semiconductor-solution (or semiconductor-overlayer) interface, and very little to the photovoltage arising from the p-n junction inside the semiconductor.

The use of semiconductors having the p-n junction in PEC cells is interesting because it has a merit in that the photovoltage is effectively generated irrespective of the presence of surface states often arising from surface defects, electrochemical reaction intermediates, *etc.* As is well known, the photovoltage at the p-n junction, together with that at the Schottky barrier, is widely used in the solid solar cells. The difference between the PEC cell and the solid cell lies in the fact that in the PEC cell the photogenerated holes (or electrons) arriving at the semiconductor surface directly react with the solution with little migration along the surface, while in the solid cell the holes (or electrons) have to travel along the surface for a macroscopic distance of a few mm until they reach the collecting grid on the cell surface. The PEC cell therefore has an advantage in that it has no restriction to have a conductive layer on the semiconductor surface so as to avoid the ohmic losses for the surface current. The photocurrent losses by electron-hole recombinations at crystal defects may also be minimized because the photogenerated holes (or electrons) coming to the surface mostly react with the solution before they drift along the surface and arrive at the defects. These advantages will be important when a polycrystalline or an amorphous material is used.

A problem, common to all semiconductor PEC cells, is that most of the available semiconductors having suitable band gaps are subject to photocorrosion in electrolyte solutions. Some trials have been made to stabilize the semiconductor electrodes. For example, an n-type silicon (n-Si) electrode was reported to be stabilized by coating with thin layers of noble metals,[8] metal oxides,[9,10] metal silicides,[11] or organic materials,[12—14] though the solar energy conversion efficiencies reported are in most cases unsatisfactory. Attempts to deposit metals on the surface for catalyzing desired electrode reactions have also been reported.[15—17]

In a recent letter[18] we reported that an n-Si electrode doped with boron from the surface and coated with a thin platinum (Pt) or palladium (Pd) layer was stable and a PEC cell with such an electrode efficiently decomposed hydrogen iodide into hydrogen and iodine under no external bias. A similar idea of photoelectrolyzing hydrogen iodide or bromide by use of electrodes composed of Si particles was proposed and high solar-to-chemical energy conversion efficiencies (6.3% in natural sunlight and *ca.* 10% by computer modelling) were reported at recent conferences by the Texas Instruments group.[19] In the present paper we will report on the electrochemical behavior of surface-boron-doped n-Si single crystal electrodes coated or not coated with a thin metal layer, together with their application to solar photoelectrolysis of hydrogen iodide.

Experimental

Two methods of boron-doping were employed: thermal diffusion and ion implantation. Thermally doped specimens were prepared from single crystal wafers of n-Si, cut perpendicular to the <111> axis and having the resistivity of 0.2 to 0.4 Ω cm and the donor (phosphorus) density of $(1-2)\times 10^{16}$ cm^{-3} obtained from Shin-Etsu Handotai Co. Chips of the n-Si wafer 0.5 to 1.0 cm^2 in area were cleaned ultrasonically in trichloroethylene, acetone, methanol, water, and 46% hydrofluoric acid, and doped with boron from the surface by coating with a saturated methanol solution of diboron trioxide (B_2O_3) and heating at 920 to 1000 °C for 0.5 to 2.0 h in the air. The chips thus doped were washed in water and etched in a 46% hydrogen fluoride (HF) solution for *ca.* 60 s.

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Specimens doped by ion implantation were obtained from Mitsubishi Electric Corp. Single crystal n-Si wafers cut perpendicular to the <100> axis and having the resistivity of 0.1 to 0.3 Ω cm were heated at 950 °C in an atmosphere of water vapor in order to cover the surface with an oxide layer *ca.* 100 nm thick, then doped by irradiating a 50 keV $^{11}B^+$-ion beam at various doses from 10^{13} to 10^{16} cm^{-2}, annealed in vacuum at 1000 °C for 20 min and etched in an HF solution.

The depth of the p-n junction formed was measured by employing the spherical drill method, namely, by slightly scraping the doped wafer with a rotating steel ball, staining by photoetching in a 46% HF solution, and inspecting the resultant concentric circles with a microscope. The p-n junction depth (x_j) was calculated from the radii of the concentric circles (R_1, R_2) and that of the steel ball (R) by using an equation $x_j=|R_1^2-R_2^2|/2R$. The sheet resistance (ρ_s) of the B-doped surface layer was measured with the four-point probe method. The surface density of boron was calculated from the above-obtained x_j and ρ_s values.[20]

A thin platinum or palladium layer was deposited by a method of thermal evaporation under $(1-2)\times10^{-5}$ Torr (1 Torr≈133.322 Pa). The Si wafer was etched in a 10% HF solution for *ca.* 60 s just before the metal evaporation. The average thickness of the metal layer was monitored with a quartz crystal oscillator. The Pt layers 2, 5, and 8 nm thick had the light transmittance at 700 nm of *ca.* 80, 50, and 30%, respectively.

ESCA spectra were obtained with a Shimadzu ESCA 750 spectrometer having a Mg *Kα* X-ray (1253.6 eV) source and a filter-type electron energy analyzer. The binding energies were corrected by taking the C1s peak as a standard, which always appeared due to sample contamination. The relative atomic concentrations were calculated from the integrated peak intensities, corrected for the relative ionization cross sections for the Si2p, O1s, B1s, N1s, I3d$_{5/2}$, Pd3d, and Pt4f peaks taken to be 0.86, 2.9, 0.49, 1.5, 19.3, 16.1, and 15.86, respectively. The depth profile was obtained by the ion etching technique using a 2.0 keV argon ion beam of a current density of 60 to 150 μA cm^{-2} under an argon pressure 5×10^{-6} Torr.

The p-n junction Si electrodes were prepared by making an ohmic contact on n-Si at the back face with indium–gallium alloy, attaching a copper wire with silver paste, and covering with epoxy resin. Current-potential curves were obtained with a commercial potentiostat and potential sweeper. The electrode not having a metal layer was in most cases etched in a 10% HF solution just before the experiment. A 120 V-300 W tungsten-halogen lamp was used as a light source, normally operated at 30 to 50 V and in some cases combined with glass filters transparent in wavelengths longer than 690 nm. Commercially available special grade chemicals were used without further purification.

Results

In the present paper, surface-boron-doped n-Si is abbreviated as p^+/n-Si. Similarly, surface-B-doped and Pt-deposited n-Si is abbreviated as Pt/p^+/n-Si, and Pt-deposited n-Si as Pt/n-Si. The depth of the p-n junction, x_j, for the thermally B-doped p^+/n-Si electrodes used in the present work was in a range from 0.3 to 1.5 μm. The surface boron concentration, c_s, determined from x_j and the sheet resistance of the doped layer took a nearly constant high value of *ca.* $(3-6)\times10^{20}$ cm^{-3}. The x_j for the B^+-ion implanted specimens ranged from 0.25 to 0.84 μm, and the c_s ranged from 10^{18} to 10^{21} cm^{-3}.

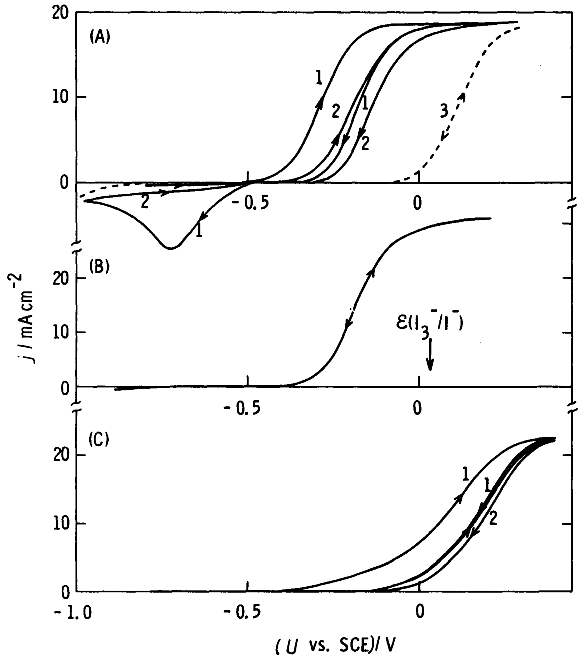

Fig. 1. Current density (j) *vs.* potential (U) curves: (A) for an n-Si electrode, 1; 1st scan, 2; 2nd scan, and 3; a curve after cyclic scanning for 60 min. (B) for a thermally B-doped p^+/n-Si electrode (x_j 0.9 μm and c_s 5×10^{20} cm^{-3}). (C) for a B^+-ion implanted p^+/n-Si electrode (x_j 0.8 μm and c_s 6×10^{20} cm^{-3}), 1 and 2 denote the 1st and 2nd scans, respectively. The electrolyte is a 7.6 M HI solution. The scan rate is 50 s/V. The illumination intensity is somewhat different in each case.

1. Photoelectrochemical Behavior of p^+/n-Si Electrodes in HI/I_2 Solutions. Figure 1A shows cyclic scanning of current density (j) *vs.* potential (U) curves for an n-Si electrode in a 7.6 M HI solution (M= mol/dm^3) under illumination. Although n-Si in this solution was more stable than in an HCl or H_2SO_4 solution, the j-U curve shifted with time toward the positive potential. The curve was restored to the initial state by dipping the electrode in an HF solution. These results suggest that the photocurrent in this case corresponds mostly to the oxidation of I^- ions and partly to the oxidation of the electrode surface.

The j-U curve for a thermally B-doped p^+/n-Si electrode (Fig. 1B) was fairly stable during the repeated cyclic scans for more than 4h, the photoanodic current corresponding to the oxidation of the I^- ions,[18] while the j-U curve for an ion-implanted p^+/n-Si electrode changed at each scan (Fig. 1C). The surface of the thermally B-doped specimens showed the presence of a dark brown, lusterless, inhomogeneous thin layer, while the ion-implanted specimens gave no presence of such a layer. The layer could be removed by oxidizing the electrode surface either photoelectrochemically or by dipping in a concentrated HNO_3 solution or heating in the air at *ca.* 850 °C followed by etching in a 46% HF solution and wiping. After such a treatment the electrode showed j-U curves similar to Fig. 1C. The x_j and c_s values were unchanged by removing the layer. The ESCA spectra of specimens having the brown layer showed that it was composed mainly of B, Si, and O atoms, the atomic ratio B/Si/O changing in a range

2/1/1 to 1/2/2 from specimen to specimen.

It is to be noted that the photocurrent for the p^+/n-Si electrode without the dark brown layer (Fig. 1C) shows very gradual increase with the potential even compared with that for the n-Si electrode (Fig. 1A). The ESCA studies of p^+/n-Si electrodes showed that they were easily oxidized only by immersing in an HI/I_2 solution in the dark for a few min, covered with a thin silicon oxide surface layer.

2. Photoelectrochemical Behavior of Pt (or Pd)/p⁺/n-Si Electrodes in HI/I₂ Solutions. Figure 2 shows *j-U* curves for a $Pt/p^+/n$-Si electrode (ion-implanted specimen with a Pt layer *ca.* 3 nm thick) in a 7.5 M HI/0.01 M I_2 solution in the dark and under illumination, together with the curve for an illuminated Pt/n-Si electrode. The similar *j-U* curves were obtained for $Pt/p^+/n$-Si electrodes prepared from thermally B-doped specimens. The photocurrent for the $Pt/p^+/n$-Si electrode was quite stable, corresponding to the oxidation of the I^- ions.[18] The difference between the potential (U_0) at which the current under illumination is zero and the redox potential of an I_3^-/I^- couple, $\varepsilon(I_3^-/I^-)$, determined from a *j-U* curve at a Pt electrode was 0.55 to 0.59 V for the $Pt/p^+/n$-Si electrodes, much larger than that for the Pt/n-Si, as seen from Fig. 2. This means that the former electrode generates a photovoltage much higher than the latter, indicating an advantage of the p-n junction.

Nearly the same *j-U* curves were obtained when Pd was deposited on p^+/n-Si instead of Pt. The electrode in this case was stable during the cyclic scanning for several hours. Figure 3 shows the relative atomic concentrations (A) as well as the binding energy for a $Pd3d_{5/2}$ ESCA peak (B) as functions of the Ar^+-ion etching time for a $Pd/p^+/n$-Si electrode which was immersed in an HI/I_2 solution in the dark after the Pd deposition. Even though a thick Pd layer had been deposited, Fig. 3A shows that most of the Pd was dissolved. The binding energy for a $Pd3d_{5/2}$ peak lay *ca.* 1.5 to 1.9 eV higher than that for pure Pd metal (Fig. 3B). Based on the reported binding energies (336.8 to 337.0 eV) for silicide-forming Pd atoms,[21] these results indicate that most of the Pd atoms left without dissolving are penetrating into the Si crystal and form silicide bonds. It is interesting to note that such a small amount of Pd is effective to stabilize the electrode and catalyze the electron transfer reaction.

Figure 4 shows the photocurrent *vs.* time for three different $Pt/p^+/n$-Si electrodes which were prepared from the same ion-implanted p^+/n-Si wafer of x_j 0.6 μm and c_s $1\times10^{20}\,cm^{-3}$, obtained under continuous illumination in a 7.5 M HI/0.1 M I_2 stirred solution, with the Si electrode connected through a resistor of 80 to 100 Ω to a Pt counter electrode. Curve A stands for an electrode having a Pt layer *ca.* 7 nm thick. The photocurrent initially increased gradually, but in about 50 h decreased suddenly. The ESCA spectra of the degraded electrode showed almost complete disappearance of the deposited Pt metal and the growth of a considerable amount of silicon oxide.

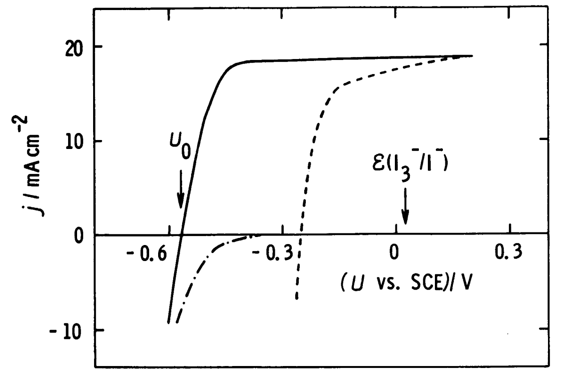

Fig. 2. Current density (*j*) *vs.* potential (*U*) curve for a $Pt/p^+/n$-Si electrode (B^+-ion implanted specimen, x_j 0.8 μm, c_s 6×10^{20} cm^{-3}, and the thickness of a Pt layer *ca.* 3 nm) in a 7.5 M HI/0.01 M I_2 solution in the dark (— · —) and under illumination (——), and the curve for an illuminated Pt/n-Si electrode (----).

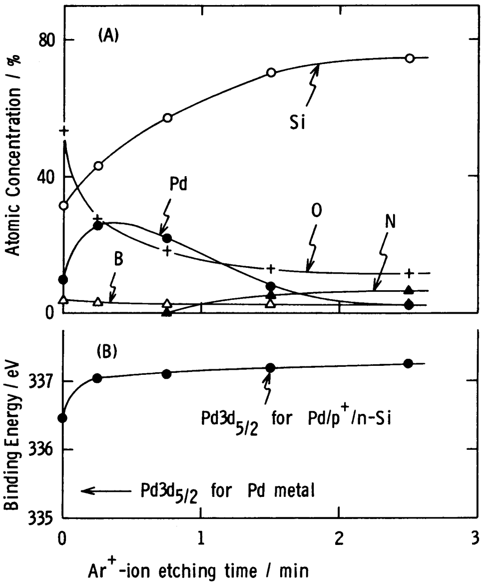

Fig. 3. Relative atomic concentrations (A) and the binding energy for a $Pd3d_{5/2}$ ESCA peak (B) as functions of the Ar^+-ion etching time for a $Pd/p^+/n$-Si electrode (thermally B-doped specimen) which was beforehand immersed in a 7.5 M HI/0.01 M I_2 solution in the dark for 40 s after the Pd deposition.

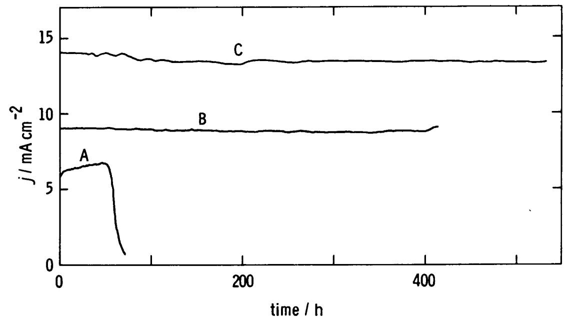

Fig. 4. Photocurrent *vs.* time curves for $Pt/p^+/n$-Si electrodes prepared from the same B^+-ion implanted p^+/n-Si wafer but coated with Pt in various ways: (A) A Pt layer *ca.* 7 nm thick as evaporated. (B) That *ca.* 7 nm thick heated at *ca.* 400 °C under (2—5)$\times10^{-5}$ Torr for 10 min. (C) Spotted Pt layers *ca.* 3 nm thick heated at *ca.* 400 °C under (2—5)$\times10^{-5}$ Torr for 6 min.

Curve B is for an electrode which was coated with a Pt layer *ca.* 7 nm thick and heated at about 400 °C under (2—5)$\times10^{-5}$ Torr for 10 min. The photocurrent in this case was steady for more than 400h. The *j-U* curves for this electrode (Fig. 5) observed before and after the stability test shows that the electrode is only slightly degraded by the prolonged illumination. The ESCA studies (Fig. 6) also show that a considerable amount of the deposited Pt still remains in this case after the prolonged illumination, though the oxygen concentration increases near the surfaces. These results indicate that the heat-treatment after the Pt deposition is effective for the electrode stabilization. It is also to be noted that the ESCA spectra of the heated and unheated specimens were almost the same, namely, the deposited Pt existed mostly in the form of pure metal, not silicide, even in the heated specimen, as seen from Fig. 6A.

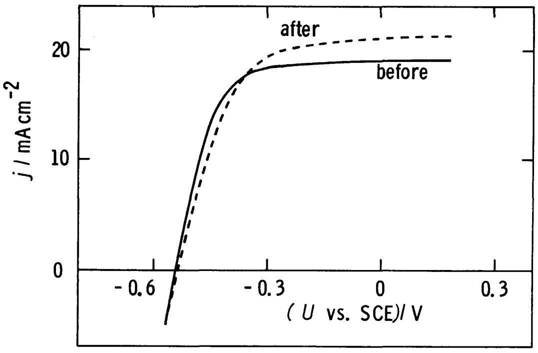

Fig. 5. Current density (j) *vs.* potential (U) curves for the Pt/p$^+$/n-Si electrode observed before (——) and after (----) the stability test shown by curve B of Fig. 4.

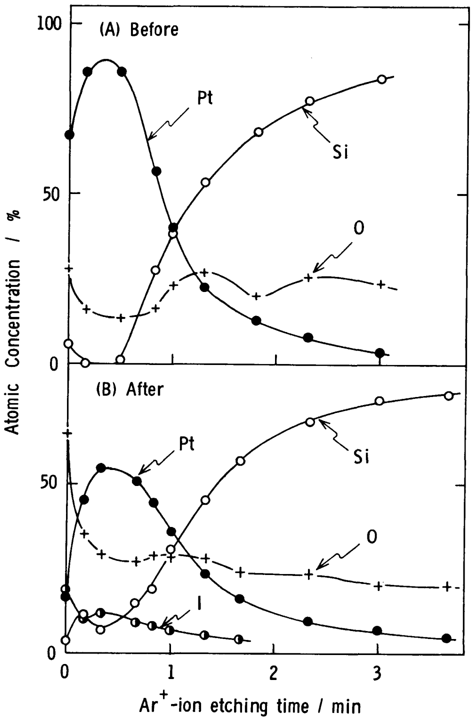

Fig. 6. Relative atomic concentrations as a function of the Ar$^+$-ion etching time for the Pt/p$^+$/n-Si electrode before (A) and after (B) the stability test shown by curve B of Fig. 4.

Curve C in Fig. 4 was obtained for a Pt/p$^+$/n-Si electrode in which the Pt was deposited through a metal net so as to form metal layers in the form of small rectangles *ca.* 3 nm thick and *ca.* 0.3 mm^2 in area, spaced *ca.* 0.7 mm from each other, followed by heating at about 400 °C under (2—5)$\times10^{-5}$ Torr for 6 min. Although the Pt layer in this case did not cover the whole surface and was considerably thinner than the case of curve B, the photocurrent was stable for more than 500 h. It was also confirmed that the photocurrent was proportional to the averaged light transmittance of the Pt layer even in the case of spotted coating.

3. PEC Cells. A number of PEC cells of a photoelectric conversion type, consisting of a Pt/p$^+$/n-Si electrode, a Pt counter electrode, and a 7.5 M HI/0.03 M I_2 stirred solution, were constructed by using various Pt/p$^+$/n-Si electrodes. With the thermally B-doped electrodes, both the open-circuit voltage (V_{oc}) and the short-circuit current (I_{sc}) were almost independent of x_j in a range 0.3 to 0.9 μm. With the B$^+$-ion implanted electrodes, nearly the same V_{oc} and I_{sc} were obtained, but the fill factor was in general somewhat better than that for the thermally doped electrodes. Under illumination of simulated AM 1 solar radiation at a power density of 100 mW cm^{-2} by use of a Wacom Solar Simulator, the PEC cells having the B$^+$-ion implanted electrodes generated the V_{oc} of 0.52 to 0.59 V, the I_{sc} of 21 to 29 mA

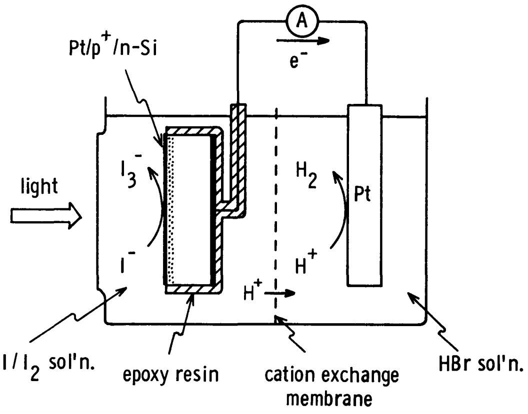

Fig. 7. A PEC cell for the HI photoelectrolysis.

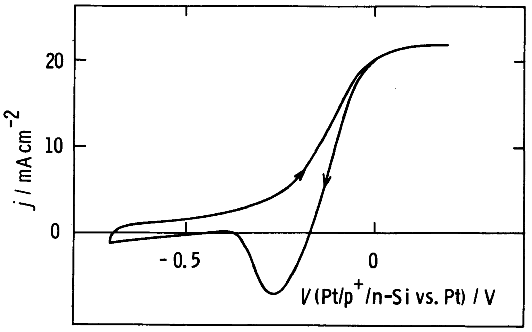

Fig. 8. Current density (j) for a Pt/p$^+$/n-Si electrode in the PEC cell shown in Fig. 7 under illumination by a simulated 100 mW/cm^2 AM 1 solar radiation as a function of the voltage externally applied between the Si and the Pt counter electrode. The curve was obtained by cyclic scanning of the applied voltage at a rate 33 mV/s.

cm^{-2}, and the fill factor of 0.52 to 0.66. The solar-to-electric energy conversion efficiencies (ϕ^{s}_{elec}) calculated were 7.1 to 9.8%. These values are considerably high if we take account of the loss of incident light intensity due to the coloration of the HI/I$_2$ solution.

PEC cells for the photoelectrolysis of HI were also constructed using a Pt/p$^+$/n-Si electrode (ion-implanted specimen, x_j 0.6 μm, c_s 1×10^{20} cm^{-3}, and the thickness of a Pt layer *ca.* 2 nm) and a platinized Pt counter electrode (Fig. 7). 2 M HI/0.01 M I$_2$ and 2 M HBr solutions were used in the anode and the cathode compartment, respectively, by taking account of the overvoltage for the hydrogen evolution in the HBr solution smaller than that in the HI solution. The solutions were separated with a commercial cation exchange membrane (Asahi Glass Co., Selemion), both half cells stirred independently. Figure 8 shows the current density (j) for the Pt/p$^+$/n-Si electrode in the above cell under illumination by the Solar Simulator mentioned above as a function of the voltage (V) externally applied between the Pt/p$^+$/n-Si and the Pt electrode. The negative applied voltage implies that the PEC cell has an electrical output even in the photoelectrolysis of HI. The current at the zero applied voltage (*i.e.*, the short circuit current of the cell) was 20.0 mA cm^{-2}. During the current flow, the solution near the Pt/p$^+$/n-Si electrode became brown or red and gas evolved at the Pt counter electrode, showing that HI was photodecomposed into H$_2$ and I$_2$ (or I$_3^-$). The change in the Gibbs energy of this reaction was estimated both from current-potential curves for the two half-cell reactions at a platinized Pt electrode and from an open circuit voltage of a fuel cell operated with the same solutions as above and one atmosphere of hydrogen gas to be 0.41 eV/ion (or 79 kJ/mol). The chemical energy stored is then calculated to be 20 mA cm^{-2}$\times$0.41 V=8.2 mWcm^{-2}, and the solar-to-chemical energy conversion efficiency (ϕ^{s}_{chem}) to be 8.2%. When a 2 M HI/0.001 M I$_2$ solution was used in the anode compartment of the cell, the short circuit current increased to 21.7 mA cm^{-2} due to the better light transmittance of the solution.

Discussion

As mentioned before, the c_s values for the p$^+$/n-Si electrodes in the present work are so high, the order of 10^{20} cm^{-3} that the B-doped p$^+$-Si layer just beneath the surface should be degenerate at room temperature,[22] namely, the Fermi level of the layer (E^{p}_{F}) lies within the valence band. This implies that the surface p$^+$-Si layer behaves like a metal. Accordingly, when a p$^+$/n-Si electrode is in an HI/I$_2$ solution in the dark, the Fermi level (E^{p}_{F}) should coincide with the redox level of the I$_3^-$/I$^-$ couple, $-e\varepsilon(I_3^-/I^-)$, with a negligibly thin Schottky barrier at an interface between the p$^+$-Si layer and the solution. It is therefore easily expected that the oxidation of the p$^+$-Si surface proceeds to some extent in an HI/I$_2$ solution even in the dark through the reaction of holes in the p$^+$-Si layer with water, followed by the hole injection by the I$_3^-$ ions. This was really confirmed by the ESCA experiments, as described before. Very gradual increase of the photocurrent at the p$^+$/n-Si electrode with increasing the potential (Fig. 1C) can be understood on the basis of the presence of such an oxide layer at the surface.

The relatively stable j-U curve for the p$^+$/n-Si electrode prepared by the thermal diffusion method (Fig. 1B) was in a previous letter[18] explained by assuming the presence of a thin Schottky-type potential barrier at a p$^+$-Si-solution interface. It has been revealed in the present work that this stability is due to the presence of a dark brown overlayer consisting of the Si, B, and O atoms. It is interesting to note that such a brown layer plays a role in preventing further oxidation of the p$^+$-Si layer, contrary to the SiO$_x$ layer which grows thicker and thicker with the passage of the photoanodic current (see Figs. 1A and C). This might suggest that the brown layer has a compact structure to be able to prevent the penetration of OH$^-$ ions or H$_2$O molecules, though the holes may pass it by tunneling or thermal hopping. Unfortunately the brown layer-covered p$^+$/n-Si electrode is not sufficient both in the stability and the photocurrent efficiency in a potential

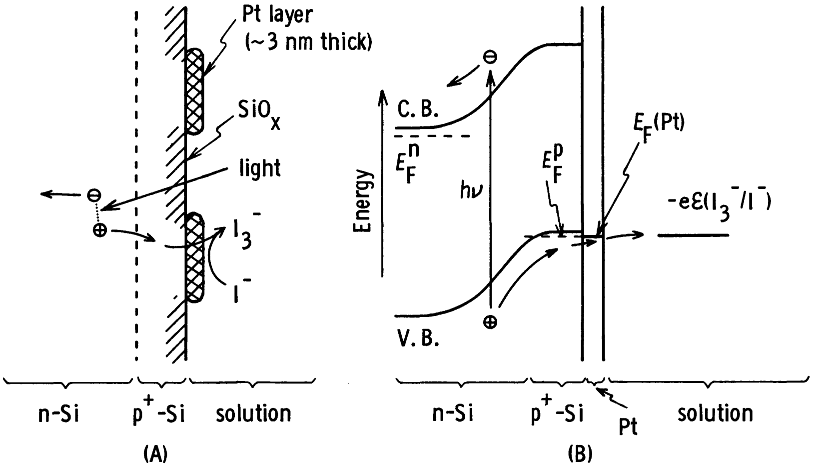

Fig. 9. Schematic cross section of a Pt/p$^+$/n-Si electrode (spotted Pt coating) in contact with an HI/I$_2$ solution (A) and energy band diagram under illumination (B). E^{n}_{F}: The Fermi level for the inside n-Si, E^{p}_{F}: that for the surface p$^+$-Si layer, and E_F(Pt): that for the deposited Pt layer. ⊖ and ⊕: Photogenerated electron and hole, respectively.

range more negative than $\varepsilon(I_3^-/I^-)$.

The p^+/n-Si electrode coated with a Pt layer is very stable in an HI/I_2 solution (Fig. 4). This is true even for *spotted coating with a relatively thin (2 to 3 nm thick)* layer (curve C in Fig. 4). In such a case, the naked parts of the p^+-Si surface must be oxidized in the HI/I_2 solution, covered with insulating SiO_x layers, as mentioned above. Therefoe the photogenerated holes must be gathered into the Pt spots and react with the I^- ions, as shown in Fig. 9. Since the p^+-Si layer just beneath the surface is degenerate, as mentioned before, and is thought to be in ohmic contact with the Pt layer, the efficient photocurrent (Fig.2) can be explained by taking account of the effective photovoltage at the p-n junction and the low overvoltage for the I^- oxidation at the surface of the Pt layer.

As described before, the Pt layer as deposited by the vacuum evaporation is not sufficiently stable, disappearing during the prolonged flow of the photoanodic current in the HI/I_2, solution, and heat-treatment is necessary for stabilization. There was no difference between the heated and the unheated Pt layer in the ESCA spectra. Possibly, some change occurred in the structure of the Pt layer. This is contradictory to the results reporting the formation of Pt-silicide by heating.[11,23] In the present work a small amount of Pt-black on a boat-shaped tungsten heater was evaporated under 2×10^{-5} Torr quickly within several to 50 s. The Si wafer thus Pt-coated was then left in the air for, say, 1 d and heated at about 400 °C under $(2-5)\times10^{-5}$ Torr by use of an electric heater covered with mica plates. It was also confirmed that the silicide was really formed when Pt was deposited slowly by a method of electron-beam evaporation under 2×10^{-6} Torr, followed by heating of the Pt-deposited Si wafer at 350 to 450 °C without exposing to the air. Anyway, we can conclude from the results of Figs. 4 to 6 that the photocurrent of the $Pt/p^+/n$-Si electrode is stable as far as the deposited Pt is left at the electrode surface.

The solar-to-chemical energy conversion efficiency ($\phi^s_{\rm chem}$) obtained in the present work for the HI photoelectrolysis is encouragingly high, 8.2%. This value is, to our knowledge, the highest of the chemical conversion efficiencies ever obtained for the PEC cells working without external bias.[13,24–28] It will still be increased by optimizing various cell conditions. We can thus conclude that the use of the p-n junction semiconductors is an effective method for the solar energy conversion by use of PEC cells. Of course, there still lie many problems for the development of the presently proposed system to a practically feasible structure.

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