

# Characteristics of Photoelectrochemical Cells Based on $n/n^+$ -Si and $p/n^+$ -Si Photoanodes Modified by Metal Films

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Photoelectrochemical cells (PECs), composed of different epitaxial  $n$ -Si photoanodes coated with evaporated metal film of Ni, Pt, Ni/Pt and immersed in solution with redox couple  $\text{Br}_2/\text{Br}^-$  or  $\text{Fe}(\text{NC})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$  were investigated. The open circuit photovoltage and short circuit current density of these PECs under optimum conditions by illuminating with a bromine-tungsten lamp ( $65 \text{ mW/cm}^2$ ), are  $0.494 \text{ V}$  and  $45.8 \text{ mA/cm}^2$ , respectively. By using a  $p/n^+$  junction for the epitaxial silicon and the Schottky barrier effect formed at the silicon-metal interface, a much higher conversion efficiency of optical to electrical energy up to  $12.3\%$  could be achieved.

## Introduction

Semiconductor PEC cells are presently the most promising devices for solar energy conversion into hydrogen by water cleavage. Silicon has been used as a selective basis for the manufacture of photoelectrodes because of its high efficiency when using it as semiconductor for photovoltaic cells, availability and its appropriate bandgap. Unfortunately, “naked”  $n$ -Si, when used as photoanode, is easily oxidized in aqueous electrolyte resulting in an insulating  $\text{SiO}_2$  layer, which causes photopassivation. Several techniques have been developed to solve this problem, Fan et al. [1–4] have demonstrated that  $n$ -Si photoelectrodes could be stabilized providing conversion efficiencies,  $\eta$ , of  $5$ – $8\%$ . Long term stabilization is also obtained by protecting the Si-surface with a thin layer of metal oxide such as  $\text{SnO}_2$  [5], ITO [6],  $\text{WO}_3$  [7],  $\text{Fe}_2\text{O}_3$  [8, 9], etc. Among them,  $n$ -Si/ $\text{Ti}_2\text{O}_3$  PECs show the highest [10] efficiency of  $11.0\%$ . Other approaches [11–16] for improvement of the photovoltage of such types of PECs can be by a  $p/n$  or  $n/p$  junction of the Si-electrode, instead of  $p$ - or  $n$ -Si ones in order to photoelectrolyze hydrogen iodide to  $\text{H}_2$  and  $\text{I}_2$  without externally applied voltage. Using in this case simulated AMI solar radiation, an energy conversion efficiency of  $6.3$ – $10.2\%$  is observed. Most of the recent

research in the photoelectrochemistry of such systems has been focused on enhancing their efficiency and stability against photocorrosion. The photoelectrochemical activity of metal or metal oxides has also been studied [17–19]. Recently was found that photoanodes of  $n/n^+$ -Si and  $p/n^+$ -Si, having a protecting layer of  $\text{NiO}(\text{OH})$ , possess considerable stability against corrosion and have a rather high efficiency of photoinduced water cleavage [20, 21].

The present work is concerned with the effect of the Schottky barrier at the metal-silicon-interface on the photovoltage and the characteristics of PECs composed of  $n/n^+$ -Si or  $p/n^+$ -Si photoanodes coated with Ni, Pt, Ni/Pt and Pt/Ni layers.

## Experimental

### 1. Production

Electrode preparation: Epitaxial silicon wafers (both  $n/n^+$  and  $p/n^+$ , junction depth  $11 \mu\text{m}$ ; resistivity of the heavily phosphorus-doped  $n^+$ -layer, epitaxial  $n$ -layer and  $p$ -layer being  $0.003$ ,  $1.1$ , and  $0.45 \text{ Ohm-cm}$ , respectively) were obtained from Shandong University Instruments Factory. The wafers with (111) orientation were etched in aqueous  $48\%$  HF solution for  $10 \text{ min.}$  and thoroughly washed with distilled water and ethanol. The known amount of metal such as Pt, Ni, etc. was quickly evaporated onto the front surface of the cleaned wafer at a reduced pressure of

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$1-2 \times 10^{-5}$  Pa. The thickness of the metal film deposited on the wafer was estimated from the optical density of a metal film deposited on a microscope slide that was placed near the wafer. The procedure of thermal treatment and fixing of an ohmic contact on the photoanodes were previously described [20, 21]. The deposited metal surface showed no obvious pits when examined with a scanning electron microscope (model S-520) at a magnification of 3000.

## 2. Photovoltaic characteristics measurements

A conventional potentiostat with a function generator (DHZ-1) together with an X-Y recorder (LZ3.204) and a digital voltmeter (PD1-A) were used for the measurement of the photovoltaic characteristics of the produced PECs.

Reagent grade chemicals were used without further purification. All solutions were prepared using at least double distilled water. A Pt-stripe was always served as counter electrode. As electrolytes were used: (I) 0.2 M KOH in the presence of 0.25 M  $K_4Fe(CN)_6$  and 0.1 M  $K_3Fe(CN)_6$ ; (II) 3.0 M KBr and 0.06 M  $Br_2$ . Before and during the experiment they were stirred by bubbling argon gas. The exposed area of the photoanode was 0.15 cm<sup>2</sup>. As a light source served a 150 W bromine-tungsten lamp combined with a 5 cm thick IR-water filter. The light intensity was measured with an absolute dynamometer (JG-1).

Electrode surface analyses of the thermally treated wafers were obtained with a spectrometer model PHI 5300 ESCA (Electron Spectroscopy for Chemical Analysis) system by using an Mg-K-X-ray source. The relative atomic ratios were estimated from the integrated peak area depending on the cyclic number of  $Ar^+$ -ion etchings. The binding energies were corrected by using the  $C_{1s}$  peak of contaminant carbon as standard.

## Results and Discussion

### 1. Photovoltage characteristics of PECs composed of $n/n^+$ -Si anode coated with films of Ni, Pt, etc.

Figure 1 shows the open circuit photovoltage ( $V_{oc}$ ) of PECs with solution I and solid state cells, both based on  $n/n^+$ -Si coated with a film of various metals, the thickness of which was ca. 6 nm. The open circuit voltage in the dark for both experimental series was almost zero. The  $V_{oc}$ -values increase distinctly with the

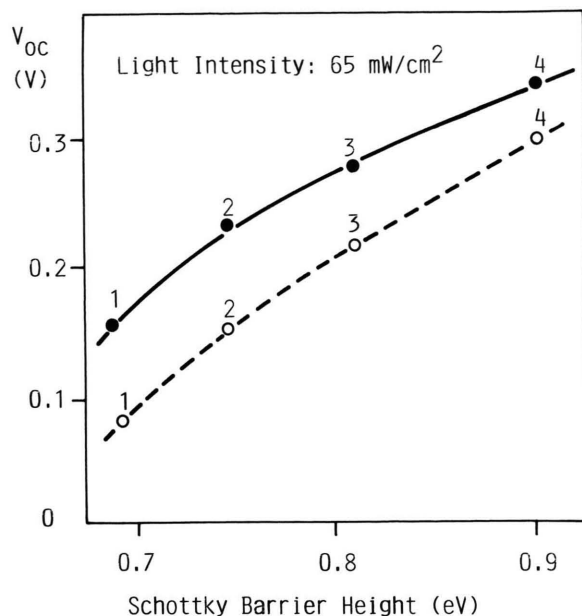


Fig. 1. Open-circuit photovoltage ( $V_{oc}$ ) of coated  $n/n^+$ -Si cells with a film (6 nm) of Ni(1), Cu(2), Au(3) and Pt(4) as a function of Schottky barrier height [22] at the metal-Si junction. (●) for PECs in solution I; (○) for solid state cells.

Schottky barrier height at the Si-metal interface [22]. An increment of ca. 0.2 V in photovoltage was observed, when Pt instead of Ni is coated on the  $n/n^+$ -Si surface. With increasing the Schottky barrier height the driving force for the following carriers increased and a better  $V_{oc}$  was obtained. The much lower  $V_{oc}$ -values of solid state cells are probably due to the lack of current collector frame on the back surface of the silicon wafer.

### 2. The characteristics of PECs composed of various anodes

Photocurrent-voltage curves for various photoanodes in solution I are presented in Figure 2A. The coated film of either Pt or Ni with ca. 6 nm thickness is made at the same experimental conditions for all photoanodes. The open circuit photovoltages ( $V_{oc}$ ) for the Pt/ $p/n^+$ -Si and Ni/ $p/n^+$ -Si are almost equal: (0.491 and 0.500 V), while those for Pt/ $n/n^+$ -Si and Ni/ $n/n^+$ -Si are quite different (0.340 and 0.158 V). It appears that in the case of  $p/n^+$ -Si, as known, the difference in Schottky barrier height between Pt/ $p$ -Si and Ni/ $p$ -Si is not very large, therefore a high photovoltage is mainly due to the  $p/n^+$  junction, which has

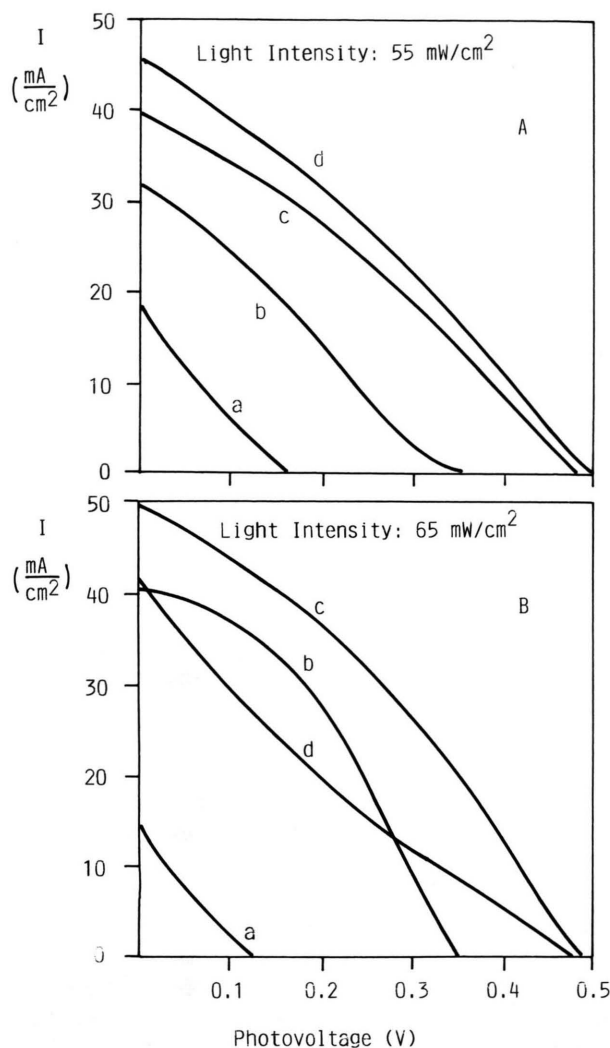


Fig. 2. (A) Photocurrent ( $I$ ) – voltage ( $V$ ) characteristics in a solution of 0.2 M KOH containing 0.25 M  $\text{K}_4\text{Fe}(\text{CN})_6$  and 0.1 M  $\text{K}_3\text{Fe}(\text{CN})_6$  for various photoanodes: (a) Ni/n/n<sup>+</sup>-Si, (b) Pt/n/n<sup>+</sup>-Si, (c) Pt/p/n<sup>+</sup>-Si and (d) Ni/p/n<sup>+</sup>-Si. (B) Photocurrent-voltage curves for photoanodes: (a) Ni/n/n<sup>+</sup>-Si, (b) Pt/n/n<sup>+</sup>-Si, (c) Pt/p/n<sup>+</sup>-Si and (d) Ni/p/n<sup>+</sup>-Si in an electrolyte of 3 M KBr and 0.06 M  $\text{Br}_2$ .

a very strong potential energy barrier. On the contrary, in the case of n/n<sup>+</sup>-Si, the Schottky barrier height between metal and silicon dominates. Obviously the Pt/n-Si barrier plays a role in enhancing the voltage. The highest photocurrent is obtained by using the Ni/p/n<sup>+</sup>-Si photoanode. Therefore Ni-silicide seems to be a catalyst for the species  $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ . Further, the cyclic voltamograms of Pt and Ni electrodes in solution I show almost the same

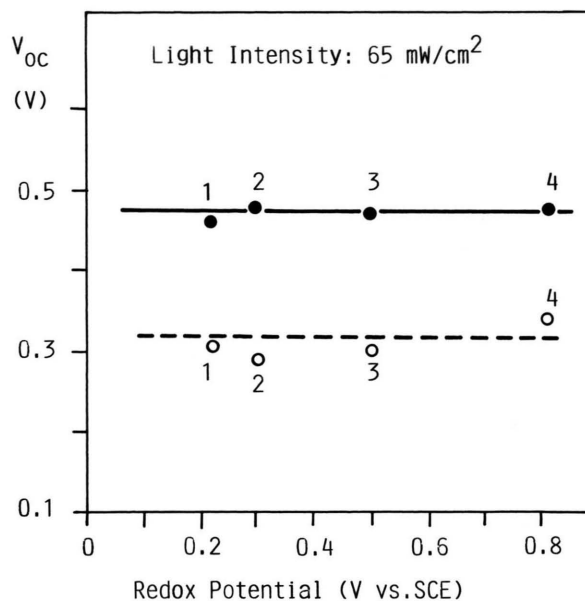


Fig. 3. Open-circuit photovoltage ( $V_{oc}$ ) vs. the potential ( $V$ ) of the redox couples on Pt/p/n<sup>+</sup>-Si (●) and Pt/n/n<sup>+</sup>-Si (○) electrodes. (1)  $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ ; (2)  $\text{I}^-/\text{I}_3^-$ ; (3)  $\text{Fe}^{2+}/\text{Fe}^{3+}$ ; (4)  $\text{Br}^-/\text{Br}_2$ .

behaviour. The photovoltaic conversion efficiencies and fill factors are found to be 1.31% and 0.25 for Ni/n/n<sup>+</sup>-Si, 5.21% and 0.26 for Pt/n/n<sup>+</sup>-Si, 10.2% and 0.29 for Pt/p/n<sup>+</sup>-Si, and 11.7% and 0.28 for Ni/p/n<sup>+</sup>-Si, respectively.

Photocurrent-voltage characteristics of the same photoanodes, but immersed in solution II are shown in Figure 2B. The variation tendency of  $V_{oc}$  in solution II is similar to that in solution I, however the photocurrents and the fill factors are rather different from those presented in Figure 2A. Much higher efficiencies and better stabilities are always obtained with Pt-coated photoanodes in solution II. This suggests that Pt film has catalytic activity for the oxidation of  $\text{Br}^-$  ions and a very good corrosion resistance.

Open circuit photovoltages of Pt/p/n<sup>+</sup>-Si (●) and Pt/n/n<sup>+</sup>-Si (○) as functions of the potential of redox couples for various electrolytes are shown in Figure 3. The  $V_{oc}$ -values for both photoanodes are essentially independent of the electrolyte redox potential. An occurrence of Fermi-level pinning at the surface implies that surface states with a high density still exist in spite of surface modifications.

In order to improve the performance parameter of the PECs, attempts were made to modify the photoanode surface by coating a Pt/Ni-bilayer onto the

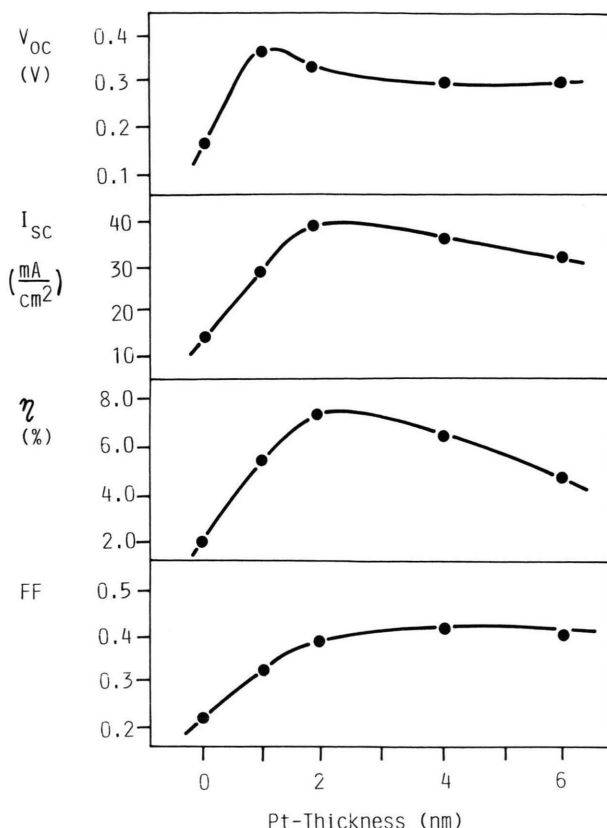


Fig. 4. Performance parameters of Ni/Pt/n/n<sup>+</sup>-Si in the aqueous solution of Fe(CN)<sub>6</sub><sup>3-</sup>/Fe(CN)<sub>6</sub><sup>4-</sup>, as functions of Pt-thickness (nm), showing open-circuit photovoltage ( $V_{oc}$ ), short-circuit photocurrent ( $I_{sc}$ ), photovoltaic conversion efficiency ( $\eta$ ), and fill factor (FF). Applied light intensity: 55 mW/cm<sup>2</sup>.

silicon wafer. Figure 4 shows the performance parameters of Ni/Pt/n/n<sup>+</sup>-Si as functions of the Pt thickness with a constant outer Ni film (6 nm). Although the highest open circuit photovoltage is obtained by coating with 1 nm Pt, the conversion efficiencies are more satisfactory when the thickness of Pt was ca. 2 nm. The fill factor apparently decreases at high thickness of Pt. The thicker the Pt-film, the less absorbance of incident light in the semiconductor occurs, causing a decrease of the performance parameters. The effect of thickness of the Ni-film on the cell parameters will be described in more detail elsewhere [23].

Some results of PECs with different photoanodes modified by Ni and Pt have been thoroughly investigated, and the obtained experimental data are compiled in Table 1. Obviously the highest  $\eta$ -values of

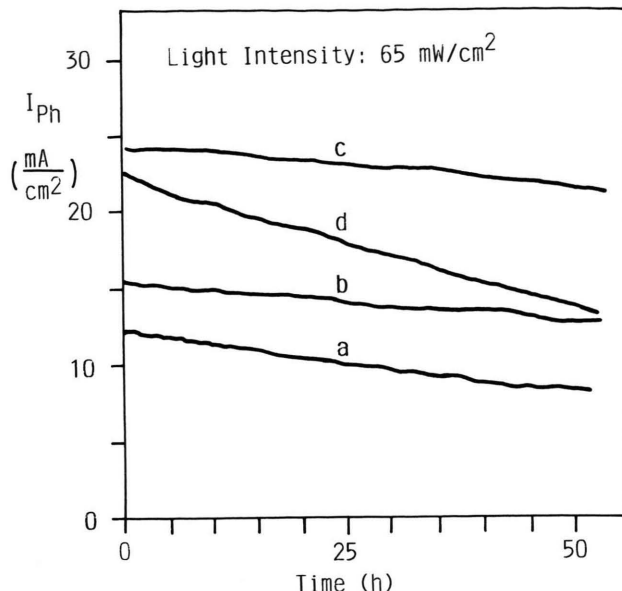


Fig. 5. Temporal stability of the photoanodes Ni/Pt/n/n<sup>+</sup>-Si (a) and Ni/p/n<sup>+</sup>-Si (d) in the solution of Fe(CN)<sub>6</sub><sup>3-</sup>/Fe(CN)<sub>6</sub><sup>4-</sup> and Pt/n/n<sup>+</sup>-Si (b) and Pt/p/n<sup>+</sup>-Si (c) in the solution of Br<sup>-</sup>/Br<sub>2</sub> with a load of 100  $\Omega$  by irradiation with a bromine-tungsten lamp.

12.22 to 12.53% were obtained with Pt/Ni/p/n<sup>+</sup>-Si electrodes.

### 3. The stability of photoanodes

According to photocurrent-time curve investigations, the photoanodes coated with Pt are neither quite stable in solution I nor in solution II, while photoanodes with outer modified Ni-film are only stable in solution I. Some representative samples, using two different electrolytes are shown in Figure 5. The photocurrent of Pt/n/n<sup>+</sup>-Si or Pt/p/n<sup>+</sup>-Si in solution II decrease by less than 10% during an operation time of 50 h (curves b and c). But, a decrease in photocurrent of about 45% for Ni/p/n<sup>+</sup>-Si (curve d) and 30% for Ni/Pt/n/n<sup>+</sup>-Si (curve a) in solution I is observed.

### 4. ESCA analysis of anode surface

The results of these studies are presented in Figure 6. Figure 6A shows ESCA results for a Ni-modified n/n<sup>+</sup>-Si sample annealed at 450°C in inert gas. There is a mixing region over a considerable distance in the whole modified layer. The binding energy for Ni2P<sub>3/2</sub> of this sample is ca. 0.4–0.8 eV higher than

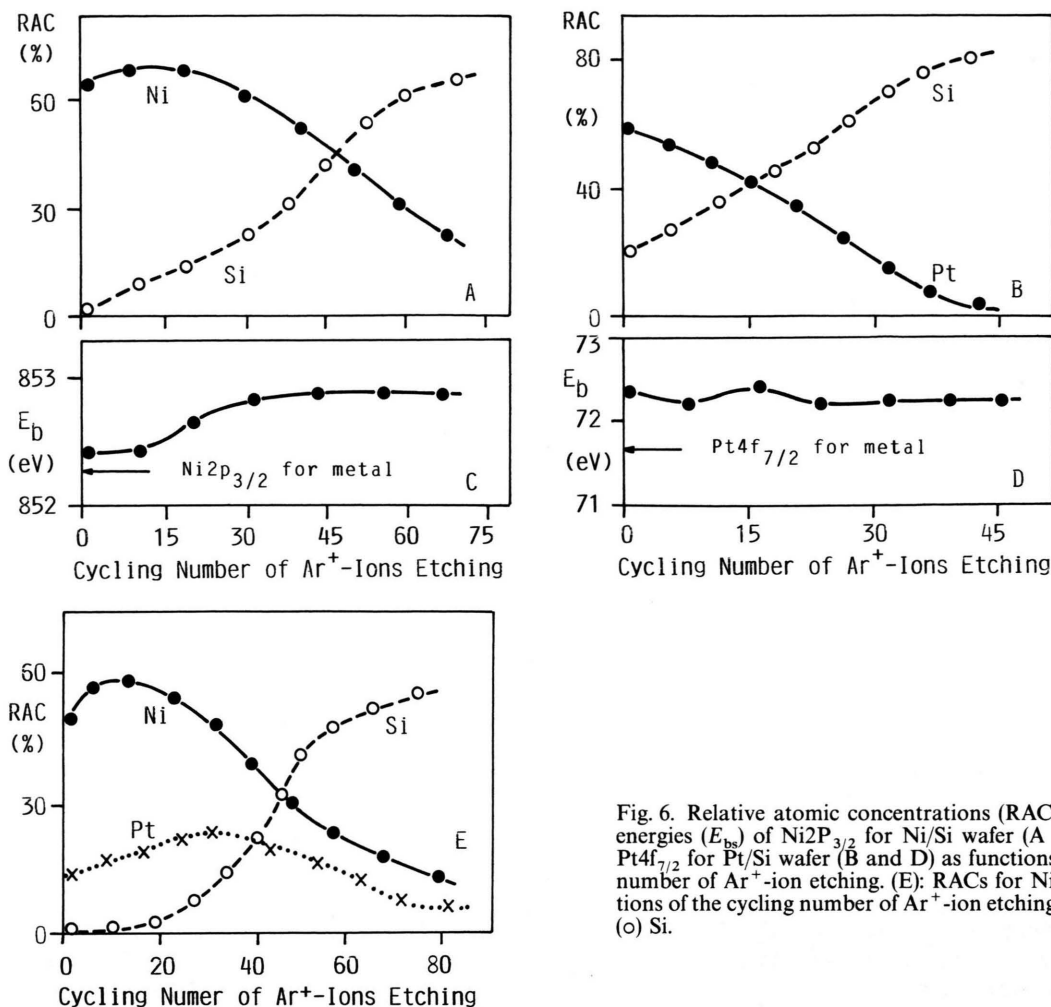


Fig. 6. Relative atomic concentrations (RACs) and binding energies ( $E_{bs}$ ) of  $Ni2P_{3/2}$  for Ni/Si wafer (A and C) and of  $Pt4f_{7/2}$  for Pt/Si wafer (B and D) as functions of cycling the number of  $Ar^+$ -ion etching. (E): RACs for Ni/Pt/Si as functions of the cycling number of  $Ar^+$ -ion etching. (●) Ni, (×) Pt, (○) Si.

Solution (Light intensity)	Photoanode	$V_{oc}$ (V)	$I_{cs}$ (mA/cm <sup>2</sup> )	$FF$	$\eta$ (%)
0.2 M KOH	Ni/n/n <sup>+</sup> -Si	0.158	18.2	0.25	1.31
0.25 M $K_4Fe(CN)_6$	Pt/n/n <sup>+</sup> -Si	0.340	32.4	0.20	5.21
0.1 M $K_3Fe(CN)_6$	Pt/Ni/n/n <sup>+</sup> -Si	0.128	20.1	0.27	1.26
(55 mW/cm <sup>2</sup> )	Ni/Pt/n/n <sup>+</sup> -Si	0.325	37.1	0.34	7.34
3.0 M KBr	Ni/n/n <sup>+</sup> -Si	0.123	14.5	0.21	0.16
0.6 M $Br_2$	Pt/n/n <sup>+</sup> -Si	0.351	40.6	0.31	8.41
(65 mW/cm <sup>2</sup> )	Ni/Pt/n/n <sup>+</sup> -Si	0.296	29.3	0.19	2.51
	Pt/Ni/n/n <sup>+</sup> -Si	0.153	26.7	0.26	1.49
0.2 M KOH	Ni/p/n <sup>+</sup> -Si	0.500	46.0	0.28	11.71
0.25 M $K_4Fe(CN)_6$	Pt/p/n <sup>+</sup> -Si	0.491	39.5	0.29	10.23
0.1 M $K_3Fe(CN)_6$	Pt/Ni/p/n <sup>+</sup> -Si	0.495	38.0	0.35	11.97
(55 mW/cm <sup>2</sup> )	Ni/Pt/p/n <sup>+</sup> -Si	0.486	35.6	0.39	12.22
3.0 M KBr	Ni/p/n <sup>+</sup> -Si	0.488	42.2	0.19	6.02
0.06 M $Br_2$	Pt/p/n <sup>+</sup> -Si	0.496	49.0	0.33	12.34
(65 mW/cm <sup>2</sup> )	Ni/Pt/p/n <sup>+</sup> -Si	0.484	42.6	0.30	9.52
	Pt/Ni/p/n <sup>+</sup> -Si	0.494	45.8	0.36	12.53

Table 1. Characteristics ( $V_{oc}$ ,  $I_{sc}$ ,  $FF$ , and  $\eta$ ) observed for PECs composed of n/n<sup>+</sup>-Si and p/n<sup>+</sup>-Si modified by Ni, Pt, Ni/Pt and Pt/Ni in different aqueous electrolytes.



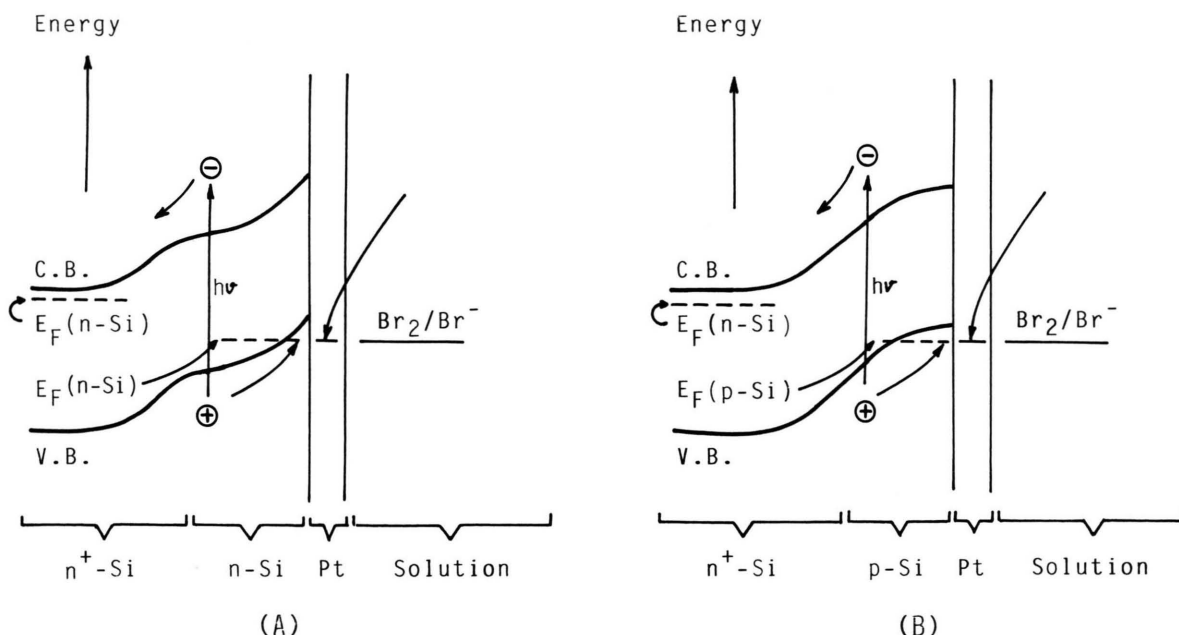


Fig. 7. Schematic representation of the relative energy levels of (A) Pt/n/n<sup>+</sup>-Si and (B) Pt/p/n<sup>+</sup>-Si.

that of pure Ni (Figure 6C). This suggests that the mixing region is composed of various nickel silicides, the bonds of which may be favourable for enhancement of the corrosion resistance of the photoanode. In case of Pt-modified n/n<sup>+</sup>-Si (6 nm Pt film annealed at 450°C) the relative atomic concentrations (RAC) and the binding energy ( $E_b$ ) for the Pt4f<sub>7/2</sub> ESCA peak are shown in Figs. 6B and D as a functions of cycling number of Ar<sup>+</sup>-ion beam etching.

It was established that the Pt atoms diffuse into Si bulk and that the Pt4f<sub>7/2</sub> peak is situated ca. 1.5 eV higher than that of pure Pt. In addition, the shift values of Si2p peak ranging from 0.3 to 0.8 eV also imply the formation of platinum silicides. No apparent difference with results reported by Nakato *et al.* [24] is observed.

Figure 6E represents the depth profile for Si-wafer coated with 6 nm as well as with 2 nm Pt film, which is annealed at 450°C. The relative atomic concentrations of Ni, Pt, and Si are given as a functions of the cycling number of Ar<sup>+</sup>-ion etching. The binding energy is not shown, it being similar as above. A weak oxygen signal is always present at the beginning of Ar<sup>+</sup>-ion etching. Therefore it is assumed that the most outer layer of the sample is NiO, followed by a layer composed of Ni- and Pt-silicides located above the bulk Si.

### 5. Energy band diagram

Typical open-circuit energy band diagrams of Pt modified n/n<sup>+</sup>-Si and p/n<sup>+</sup>-Si electrodes are given in Figure 7. The extent and shape of the band bendings for the two electrodes are different. The band bending for (A) is mainly due to the sum of the n/n<sup>+</sup>-junction height and the Pt/n-Si barrier. The situation in Fig. 7B may be attributed to the p/n<sup>+</sup>-junction, whereas Pt/p-Si is regarded as an ohmic contact. It has been estimated by means of a relation according to [25] that the difference in the barrier height of the p/n<sup>+</sup>- and n/n<sup>+</sup>-junctions is ca. 0.71 V. The barrier height of Pt-Si on n-Si is 0.85 V [22]. Thus, the difference in the extent of band bending for Figs. 7A and B may be not too large. As to the open circuit photovoltage of the respective PECs, the difference between them was found to be ca. 0.14 V, as indicated in Table 1.

### Conclusion

- It was found that the open-circuit photovoltage ( $V_{oc}$ ) increases distinctly with the barrier height at the interface of silicon/metal.
- The effect of Pt/Ni or Ni/Pt dual film annealed at 450°C on the surface of PECs composed of n/n<sup>+</sup>-Si

and p/n<sup>+</sup>-Si is of advantage, leading to an increase of the open-circuit photovoltage and of the photoanodes stability.

– The PECs composed of epitaxial silicon anode coated with metal silicide film possess much higher efficiency for conversion of optical to electrical energy, amounting up to 12.5%. This technology might be a candidate for practical application of photoelectrodes for water cleavage by solar energy.

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