

Semiconductor Electrodes

XLVI. Stabilization of n-Silicon Electrodes in Aqueous Solution Photoelectrochemical Cells by Formation of Platinum Silicide Layers

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The stabilization of small bandgap semiconductors against photocorrosion in photoelectrochemical (PEC) cells is necessary in the design of practical cells for the conversion of solar energy to electricity, and is of critical importance in photoelectrosynthetic systems where the photogenerated holes produce highly oxidizing species (e.g., Br_2 , O_2 , Cl_2 , etc.) at the semiconductor surface. One approach involves the utilization of thin films of metals (1) or semiconductors (2) to protect the surface. The deposition of conductive polymer layers (3) or protective polymer films (4) on the semiconductor surface can also decrease the rate of photocorrosion. Highly stable n-Si photoelectrodes can be achieved by coating the photoanode with a thin gold or platinum layer overcoated with a thick polypyrrole (PP) film (5). The increased stability can mainly be attributed to the rapid interfacial charge transfer kinetics between Si and the (metal/PP) overlayer and those between the (metal/PP) layer and solution species (6).

There is a wealth of information concerning thin film-semiconductor reactions, especially metal thin films on silicon (7,8). Metals deposited upon Si can react to form various compounds, which exhibit metallic conductivity, good mechanical adhesion, and reasonable chemical stability. We report here a study of the electrochemical (EC) and PEC behavior of silicide-coated silicon electrodes in aqueous solution, and amplify our preliminary report (9) of the stable PEC performance of such electrodes in aqueous solutions containing several redox couples. We demonstrate that Pt silicide coated n-Si electrodes can be employed to fabricate stable PEC cells with aqueous solutions containing various redox couples, e.g., $\text{Fe}^{2+}/\text{Fe}^{3+}$, I^-/I_3^- , $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$. Power conversion efficiencies of 5 to 8% at $65 \text{ mW}/\text{cm}^2$ irradiation from a tungsten-halogen

lamp can be achieved by choosing a suitable redox solution and by optimizing the conditions used to prepare the silicides.

Platinum silicides were prepared by procedures reported previously (8). N-Si single crystals (0.4 to $0.6 \Omega\text{cm}$) donated by Texas Instruments were ultrasonically cleaned in trichloroethylene, acetone, and methanol. Immediately prior to vacuum deposition of platinum, the n-Si crystals were etched twice with 48% HF solution for 10 min. The etched crystals were then rinsed thoroughly with distilled water and methanol and dried in vacuum. The platinum films were deposited by flash evaporation of a known amount of Pt on the n-Si crystals at a pressure of 10^{-6} torr. The thickness of the Pt film deposited was calibrated spectrophotometrically. Immediately after metal deposition, the Pt-coated n-Si crystals were annealed *in situ* at about 400°C for 5-15 min. at a pressure of 10^{-6} torr. The crystals obtained showed a mirror-like surface with no obvious pits when examined at a magnification of 500X.

The detailed procedures for preparing the ohmic contacts, mounting and sealing the electrodes are similar to those previously reported (5a). The voltammetric experiments and the solar cell measurements were performed with the same apparatus and procedures as reported previously (10). The light source used in the study of the PEC effect was a tungsten-halogen lamp fitted with a 13 cm thick water filter. The Auger electron spectroscopic (AES) measurements were performed with a Physical Electronics 590 system. Reagent grade chemicals were used without further purification. All solutions were prepared from triply distilled water. All experiments were carried out with the solution under a nitrogen atmosphere.

The Auger depth profile (Fig. 1) of the annealed specimen of Pt on n-Si showed that at the surface, a significant amount of Si, oxygen and Pt existed. At increasing sputter times the oxygen signal quickly disappeared and the Pt signal increased with increasing depth for the first 20 Å. Near 20 Å, the

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signal due to the oxygen vanished; on the other hand, a significant Pt signal remained to a depth of about 80 Å. The Si signal increased steadily up to a depth of about 80 Å. Thus Pt diffuses into the Si for a considerable distance and does not merely form an adlayer on the surface. Oxygen (perhaps from the thin native oxide layer) remains right on the surface and does not diffuse deeply into the Si substrate.

The current-voltage curve for an n-Si electrode, which was coated with about 40 Å of Pt and annealed at 400° C at 10^{-6} torr for 10 min., in a solution containing 1 M FeCl_2 , 0.1 M FeCl_3 , and 1 M HCl under illumination of 65 mW/cm^2 (tungsten halogen lamp) is shown in Fig. 2. The initial short-circuit current density is 16 mA/cm^2 , the open-circuit voltage is 0.38 V and the fill factor 0.62. The maximum power conversion efficiency is thus 5.8%. Stability tests (Fig. 3) under illumination of 65 mW/cm^2 showed no deterioration in short-circuit current, a slight increase in open-circuit voltage, and about a 10% decrease in the fill factor (ff) after 20 days of discontinuous illumination with the passage of about 10,000 C/cm^2 . No apparent change in the electrode surface was observed after this extended irradiation under a magnification of 500X.

A better fill factor was observed for I^-/I_3^- (ff = 0.72) and $\text{Fe}(\text{CN})_6^{3-}/4^-$ (ff = 0.70) couples. Under similar illumination conditions, these three couples show essentially the same open-circuit voltage. However, $\text{Fe}(\text{CN})_6^{3-}/4^-$ gives the highest short-circuit current density (ca. 20 mA/cm^2) and I^-/I_3^- the lowest (ca. 13 mA/cm^2) (perhaps because of solution absorption of incident light by I_3^-).

In conclusion, Pt silicide-coated n-Si electrodes have been shown to give highly stable PEC performance in aqueous solutions. The exceptional stability and performance of these PEC cells might be due to the following: (1) fast interfacial charge transfer kinetics between the n-Si substrate and the platinum silicide and between platinum silicide and solution redox species; (2) separation of region of photocharge carrier generation from solution contamination; (3) good mechanical stability of the silicide on the silicon substrate; (4) reasonable chemical and electrochemical stability of the silicide. Detailed EC and PEC studies on different silicide-coated electrodes and suitably modified forms of these electrodes for the stable photooxidation of Br^- , Cl^- and H_2O will be published elsewhere.

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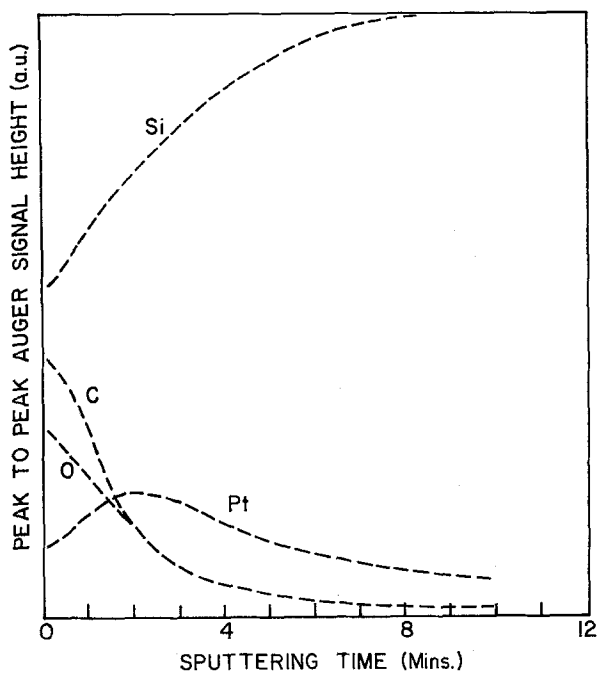


Fig. 1: Auger depth profile of annealed specimen of Pt on n-Si. Pt thickness deposited $\sim 40 \text{ \AA}$. Annealing temperature 400°C at $\sim 10^{-6}$ torr for 15 min. Sputtering rate $\sim 10 \text{ \AA}/\text{min}$.

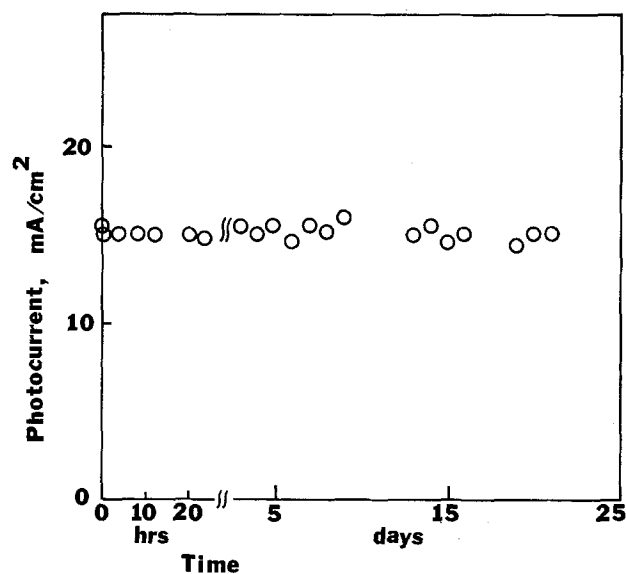


Fig. 3: Photocurrent-time behavior of platinum silicide coated n-Si electrodes illuminated with tungsten-halogen lamp at $65 \text{ mW}/\text{cm}^2$ at biasing potential at 0.4 V vs SCE. Solution and electrode are similar to those used in Figure 2. Illumination time per day ranged from 4 to 24 hours.

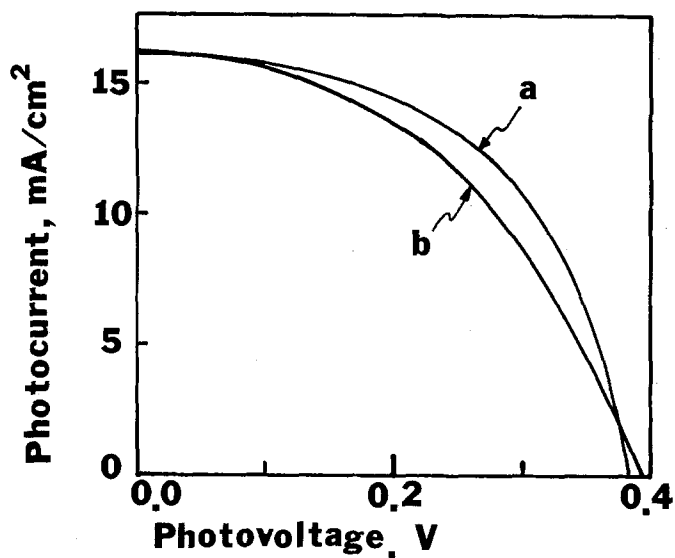


Fig. 2: Photocurrent-photovoltage characteristics of the cell n-Si (Pt silicide coated)/ 1.0 M FeCl_2 , 0.1 M FeCl_3 , $1 \text{ M HCl}/\text{Pt}$ at $65 \text{ mW}/\text{cm}^2$ illumination. Pt thickness deposited $\sim 40 \text{ \AA}$. Annealing temperature 400°C at $\sim 10^{-6}$ torr for 10 min. (a) Before long-term stability test. (b) After long-term stability test.