

Enhanced Photoelectrochemical Behavior of Gold-coated Porous n-Si Electrochemically Modified with Polyaniline

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Abstract : The presence of a porous Si layer(PSL) formed on the surface of crystalline silicon by electrochemical etching in HF solution is found to enhance the stability of n-Si photoanodes, but porous n-Si thus formed is still liable to corrode upon exposure to excitation light. To improve the stability of the porous n-Si electrodes and to reduce the photo-induced corrosion, we have examined the PEC behavior of porous n-Si modified with polyaniline(PANI) and 3 nm thick layer of Au. Comparisons were made between Au/PSL and PANI/Au/PSL photoelectrodes.

Keywords : photoelectrochemical(PEC) solar cell, porous n-Si, photocurrent-voltage, polyaniline(PANI)

1. Introduction

Porous silicon, formed by chemical and electrochemical etching in hydrofluoric acid, has attracted considerable attention in recent years by many investigators[1]. These investigations are almost related to the electropolishing of silicon to process silicon wafers for the electronic device[2], and the fabrication of silicon microstructures[3] and silicon-on-insulator structures[4]. However, the recent attempts are focused on photoluminescence[5] and electroluminescence[6] at room temperature, and photoelectrochemical(PEC) cells

for the solar-energy conversion[7]. It is still important to develop new approaches to high efficiency and low cost solar cells.

The porous silicon layer(PSL) fabricated by electrochemical anodization in HF solution is especially useful for producing an efficient PEC cell because of the increase in the active area and decrease in the reflection loss of the incident light. The PSL consists of a great number of nanometer-size pores(2~10 nm in diameter) and has a 20~80 % porosity[8]. These nanocrystallites of PSL are known to increase its own band gap due to the quantum-confinement effect[1(c)]. Mao et al.[7(c)] recently reported an efficient($\eta = 7.9$

%) PEC solar cell using an electrochemically etched p-Si electrode in a nonaqueous redox electrolyte solution. But photodegradation of the PSL still occurs, especially in an aqueous solution. Modifying surfaces of various photoelectrodes which have narrow band gaps with transparent thin metal films[9] and conducting organic polymers[10] has been used to stabilize the substrate against photocorrosion in aqueous and nonaqueous solutions.

In this paper, we attempt to enhance the efficiency of solar-energy conversion and stability in aqueous solution by using electrochemically fabricated PSL electrode as a photoanode, which is additionally modified by coating of metal and/or conducting polymer such as Au and polyaniline(PANI)[11], respectively. With PANI / Au / PSL electrodes, the efficiency obtained to be as high as 7.1 % and the stability of PEC solar cell is much more enhanced compared with an n-Si anode.

2. Experimental

2.1. Preparation of PSL electrodes

The PSL formation was made by anodizing phosphor doped, (100) oriented, and 5 ~ 20 Ω cm resistivity n-type silicon wafers with a mirror surface(Siltron Inc.). The wafers were cleaned to remove an organic impurity and an oxide layer with conc. H_2SO_4 / 35 % H_2O_2 (2:1) for 10 min and H_2O / 50 % HF(10:1) for 10 ~ 15 sec, respectively, followed by rinsing with doubly distilled water and drying under N_2 stream. Ga-In eutectic was rubbed on a back side of the clean wafer in order to form ohmic contact with a Cu plate which was then soldered with a Cu wire. To limit the PSL electrode area, the exposed wafer was covered with an epoxy(K-poxy, Mckim Group) except for 0.1

cm^2 . Anodization of the thus prepared n-Si electrodes was carried out in a 50 % HF / $\text{C}_2\text{H}_5\text{OH}$ / H_2O (1:1:1) solution using a Pt-gauze as a counter electrode at a constant current density under 90 mW/cm^2 illumination. The light source was a 200 W quartz tungsten halogen lamp(QTH; Oriol) fitted with a water jacket. The anodic current density to anodize the n-Si electrode was adjusted to 1 ~ 10 mA/cm^2 . Uniform PSL was obtained when the etching solution was stirred slowly. After anodizing the Si electrodes, the HF etchant left in PSL was dried under a steam of N_2 after rinsing with ethanol and distilled water.

2.2. Modification of PSL electrodes

Gold film was coated thermally on PSL using a Leybold L560 vacuum evaporator at 1.5×10^{-8} bar. Typical thickness of gold film was about 3 nm. Electropolymerization of aniline on Au-coated PSL electrode was performed from 5.0×10^{-2} M aniline in 2.0 M H_2SO_4 solution using a PAR 273 potentiostat under 80 mW/cm^2 illumination intensity. The polymerization was observed at potential between -0.15 ~ +0.50 V(vs. Ag/AgCl). The formed PANI films were transparent-yellowish and exhibited a good adherence to the Au/PSL electrode, unlike the case of nonmodified bare n-Si where the deposited films were easily removable by mechanic stresses.

2.3 Measurements of photocurrent-voltage

The modified n-Si electrodes were illuminated in a two-electrode one-compartment cell with a Pt gauze serving as the counter electrode, and photocurrent-voltage measurements were performed using a Keithley 236 source-measure unit. The solution were stirred during PEC measurements. The solutions used for the PEC experiments contained the redox couple 0.50 M FeSO_4 and 0.15 M $\text{Fe}_2(\text{SO}_4)_3$ in 0.10 M H_2SO_4 unless otherwise specified.

3. Results and Discussion

Fig. 1 compares typical J-V curves for the PSL electrodes that were electrochemically fabricated in HF-ethanol mixture. The curves Fig. 1(a) and Fig. 1(b) are those for the PSL electrodes coated with a 3 nm thick Au(Au/PSL) and for the electrode(PANI/Au/PSL), respectively. They were measured in a gently stirred solution of 0.50 M FeSO_4 and 0.15 M $\text{Fe}_2(\text{SO}_4)_3$ containing 0.10 M H_2SO_4 as supporting electrolytes. The J-V curves are strikingly improved after coating with Au on PSL and PANI on Au/PSL. The typical open-circuit photovoltage(V_{OC}) for a PANI/Au/PSL electrode was 0.45 V, as is shown by the curve (a) in Fig. 1, which shows the short-circuit photocurrent(J_{SC}) of 29.3 mA/cm^2 , fill factor(FF) of 0.51, and conversion efficiency(η) of 7.4 % under irradiation at 93 mW/cm^2 . Because we did not take into account the loss of illumination intensity due to light absorption by the 7 cm water filter and the redox electrolytes, the intrinsic efficiencies of PSL electrodes are actually higher than the observed values.

In the case of bare PSL(the curve (c) in Fig. 1) J_{SC} is only of 2.5 mA/cm^2 , but V_{OC} is 0.78 V. The small J_{SC} is attributed to the photodegradation of a fresh bare PSL whose progress is fast especially in aqueous solution. The possible antireflection characteristics of PSL is apparently overwhelmed by the rapid photodegradation. Nonmodified PSL electrodes in the present work gave V_{OC} s of 0.7 to 0.8 V, which are much higher than those(0.38 ~ 0.45 V) for the PEC cells equipped with Au/PSL and PANI/Au/PSL electrodes. The reason for the decrease in V_{OC} after Au modification is that the PSL surface of which electron affinity is 4.0 eV becomes electrostatically equilibrated with Au of which work function is 5.1 eV. In this rectifying junction between a metal and an n-type semiconductor, called a Schottky barrier diode, electrons from the semiconductor flow into the lower energy states in metal when work function of metal is larger than electron

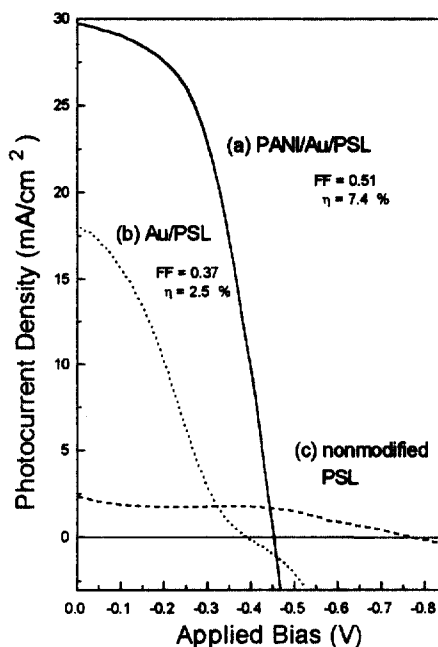


Fig. 1 J-V curves of modified PSL electrodes in 0.10 M H_2SO_4 containing 0.50 M FeSO_4 and 0.15 M $\text{Fe}_2(\text{SO}_4)_3$. The light intensity was 93 mW/cm^2 .

affinity of n-type semiconductor[12]. Positively charged donor atoms remain in the semiconductor creating a space charge region (depletion region). As a result, the photogenerated electrons can experience more surface recombination, which is expected to decrease V_{OC} .

The stability of the n-Si photoanodes in aqueous solution is greatly improved by the modification with Au and PANI. Fig. 2(a) and 2(b) show the time dependence of J_{SC} and V_{OC} of various PSL electrodes, respectively. It is clear that both J_{SC} and V_{OC} of the modified PSL electrodes are more stable than those of the nonmodified PSL electrode. The J_{SC} of PANI/Au/PSL electrode decayed by only 5 %, while that of Au/PSL electrode decreased to 27 % from the initial value for 6 hour period. Although Au films were attached firmly to PSL, it appears that all the surface of PSL is not coated with Au. PANI films which was attached well on Au/PSL and PSL further improve the

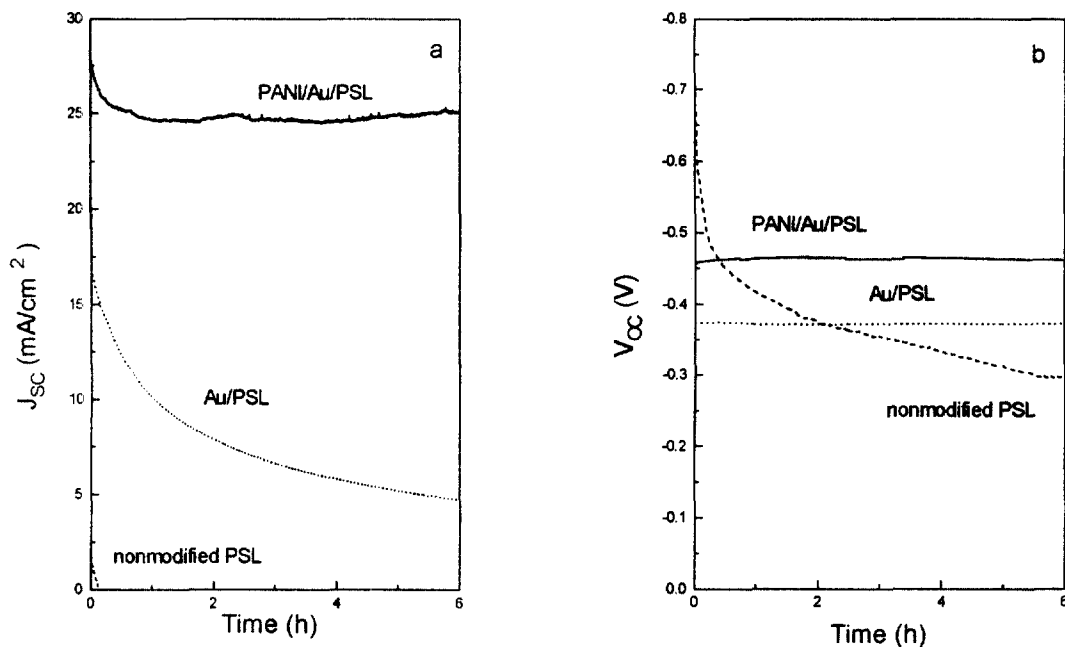


Fig. 2 Time dependence of short-circuit current(a) and open-circuit voltage(b) of modified PSL electrodes under the same condition as in Fig. 1.

stability of J_{sc} . The decrease in V_{oc} with time is also much smaller for both of the electrode modified by PANI/Au or Au on PSL than for the nonmodified bare PSL electrode. The present results in water clearly indicate that Au and PANI/Au films stabilize PSL photoanodes against degradation. As discussed previously for electrochemically etched p-Si in acetonitrile[7(c)], the decay of the photocurrent with time is attributed to the growth of insulating oxide layers arising from the surface reaction of Si with photogenerated holes and trace water. The modified PSL electrodes coated with Au and PANI are protected from corrosion and enhance the transfer of the photogenerated holes, h^+ , to solution in aqueous electrolyte solutions. This protection can suppress insulating oxide layers to be formed by the reaction of the radical structures of silicon with water on PSL surfaces. The radical structures of silicon are produced by h^+ in the valence band[1(c)]. The more effective

results are observed with PANI/Au/PSL photoanodes since the Au film grown under the present work did not cover all the PSL surface.

The J_{sc} of the PANI/Au/PSL photoanode exhibits a nonlinear dependence on the light-intensity as shown in Fig. 3(a). At low light intensities, J_{sc} increased in direct proportion to illumination intensity, but it deviated from the linearity above $20 \text{ mW}/\text{cm}^2$, and eventually appeared leveled off at higher illumination level. The leveling off of J_{sc} with increase of light-intensity can be attributed to a charge-transfer-limitation occurred due to the restricted transfer of photogenerated h^+ from silicon to the redox couple in solution. Furthermore, V_{oc} also showed a monotonic increase with illumination intensity. In Fig. 3(b), conversion efficiency, η , shows a broad maximum near $40 \text{ mW}/\text{cm}^2$ illumination-level. The η is defined as

$$\eta = \frac{J_{sc} \cdot V_{oc} \cdot FF}{P_{in}}$$

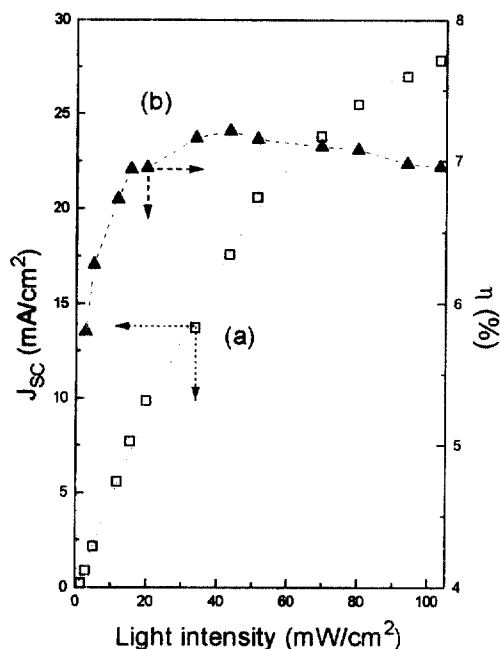


Fig. 3 Light- intensity dependence of J_{sc} and η of a modified PANI/Au/PSL electrode under the same condition as in Fig. 1.

where FF is a fill factor and P_{in} is the incident light intensity. The existence of a maximum in η with increase of illumination-intensity albeit the increases in V_{oc} and J_{sc} suggests that the FF is decreasing. Indeed, from the J-V curves the FF of the PANI/Au/PSL electrode showed a continuous decrease from 0.56 at 3 mW/cm^2 to 0.25 at 103 mW/cm^2 .

The V_{oc} s of PANI/Au/PSL electrodes were found to be 0.36 ± 0.02 V, regardless of the a type of redox couples as shown in Fig. 4, and other characteristics are summarized in Table 1. Fig. 4 demonstrates that the V_{oc} s of PANI/Au/PSL photoanode exhibit Fermi level pinning. This Fermi level pinning limits to obtain of a photoelectrode of a larger V_{oc} , but makes possible to use a various kinds of redox couple in a PEC cell. The Fermi level pinning implies that the energy levels of the electrodes surface are shifted with respect to the energy

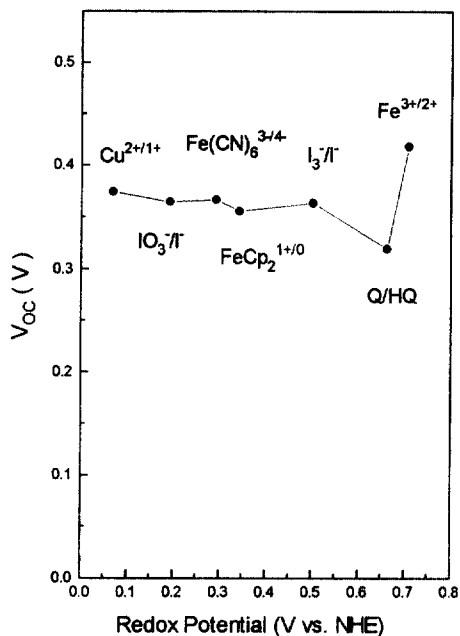


Fig. 4 V_{oc} of a PANI/Au/PSL electrode as a function of the redox potential of the electrolyte.

Table 1. Photoelectrochemical characteristics of a PANI/Au/n-Si electrode in 0.2 M H_2SO_4 containing a redox couple.

redox couple	J_{sc} (mA/cm^2)	V_{oc} (Volt)	FF	η (%)
$Cu^{2+}/1+$	8	0.37	0.38	1.1
IO_3^-/I^-	6	0.36	0.44	1.0
$Fe(CN)_6^{3-/4-}$	2	0.36	0.31	0.18
$FeCp_2^{1+/0}$	1.7	0.35	0.56	0.24
I_3^-/I^-	10	0.36	0.27	0.98
Q/HQ	15	0.34	0.24	1.0
$Fe^{3+}/2+$	36	0.42	0.34	5.2

levels in solution. A recent study demonstrates that the band edge shift can account for the sigmoidal shape of the J-V curves of PEC cell[13]. As shown in Table. 1, the FF factor, which is a qualitative measure of the

deviation of the J-V curves from ideal square-like to sigmoidal shape, varies considerably, supporting the shift of the band edges.

In conclusion, the electrodes modified with Au and PANI layers on porous n-Si surface block the electrolyte from contacting n-Si directly in aqueous H₂SO₄ solution and helped to derive rapid removal of photogenerated charge carriers from n-Si surface before reacting with the electrode material. Au coating alone was not sufficient to protect porous n-Si from photocorrosion in aqueous solution. The PANI/Au/PSL electrode showed a continuous decrease in the FF with the increase of light intensity, indicating that the band edge of the electrode shifts. The shift is supported by the observation that the V_{OC} remained nearly constant irrespective of the kind of redox couples over a wide range of redox potentials.

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