

RECTIFYING EFFECT OF POLYANILINE(PANI)/N-TYPE POROUS SILICONE HETEROJUNCTION*

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Abstract Heterojunctions between polyaniline (PANI) and *n*-type porous silicon (PS), Al/PS-PANI/Au cell, were fabricated, and the rectifying parameters of this heterojunction diode were measured as a function of the preparation conditions of PANI and PS, the electronic structure of PANI as well as cell structure. The rectifying parameters of Al/PS-PANI/Au cell were determined to be $\gamma = 1.8 \times 10^1 \sim 1.0 \times 10^5$ for the rectifying ratio at 3V, $n = 3 \sim 12$ for the ideal factor, $j_0 = 8.0 \times 10^{-5} \sim 5.6 \times 10^{-2}$ mA/cm² for the reversed saturated current density, and $\phi_b = 0.67 \sim 0.83$ V for the barrier height, respectively. The best rectifying heterojunction diode made between PANI and *n*-type PS with higher rectifying factor ($\gamma = 1.0 \times 10^5$ at 3V), output current (>1500 mA/cm² at 3V) and lower ideal factor ($n = 3.3$) was obtained by preventing the oxidation of PS before evaporating Al electrode.

Keywords Polyaniline (PANI), Porous silicon (PS), Rectifying effect, Heterojunction

INTRODUCTION

The rectifying diode, as an electronic device, is based on either the Schottky effect or *p-n* junction. The former is made between semiconductor and metal, while the latter is made between *p*-type and *n*-type semiconductor. Recently, porous silicon (PS), as a highly efficient visible photoluminescence material^[1], has attracted attention because of its potential applications in electroluminescence (EL). In addition, polyaniline (PANI), as a *p*-type conducting polymer, is a good candidate for fabricating such electronic devices. The reasons for this are as follows: (1) Its room-temperature conductivity varies between insulator and metal by proton doping^[2], (2) A transparent conducting film or layer of PANI has been fabricated^[3], which is very important for a device involving PS in order to allow optical emission; and (3) PANI is quite stable in air, which is a key requirement for its application in technology. Thus, it is expected that the heterojunction rectifying diode made between PANI and PS can be fabricated.

In this article, the *p-n* heterojunctions (Al/PS-PANI/Au cell) were fabricated, by preparing the PANI films by dipping polymerization or spin coating. This heterojunction diode was measured as a function of the preparation conditions of PANI and PS, the protonation state of PANI and the cell structure.

EXPERIMENTAL

The cell structure of heterojunction diode made between *p*-type PANI and *n*-type PS is shown

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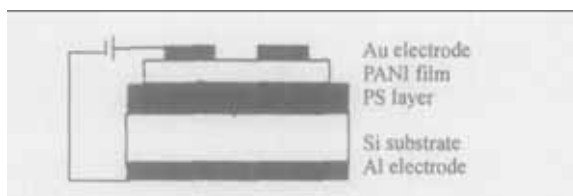


Fig.1 The cell structure of heterojunction diode made between PANI and PS

in Fig.1. The preparation of the PANI film, the PS layer on the silicon substrate and the metal electrode are described as follows.

PS Layer on the Silicon Substrate

n-Type silicon substrate (doped with *P*, $6 \times 15 \text{ mm}^2$, 0.51 mm thick and $\rho = 3 \sim 5 \Omega \cdot \text{cm}$.) was used in its original form, without further treatment. A thin layer of PS on the silicon substrate was anodized electrochemically in a HF solution (40% HF:ethanol = 50:50/vol.%) at a constant current of 3 mA/cm^2 for 10 min, followed by immersing it in the HF solution for 1 min. Then the Si plate with the PS layer was drawn out and washed with deionized water, and dried with nitrogen. Atomic force microscopy (AFM) images show that the PS layer is uniform with 3–6 nm in diameter as shown in Fig.2.

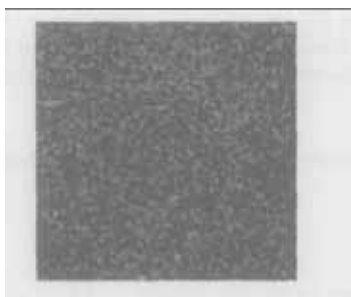


Fig.2 The morphology of PS measured by AFM method

Thin PANI Film Coated on PS

Two methods, dipping polymerization and spin coating, were used to prepare thin PANI films on the surface of PS. An aniline monomer was distilled under reduced pressure while ammonium persulfate as oxidant was used in its original form without further treatment. In the method of dipping polymerization, the resulting PS substrate is dipped in the aniline monomer (0.15 mol/L) containing hydrochloride (1.0 mol/L HCl) solution, and an equal volume of 0.075 mol/L ammonium persulfate is added. By this method, a thin transparent conducting PANI film ($\sigma_{\text{RT}} \approx 5 \text{ S/cm}$) coated on the PS substrate obtained after several minutes. Then wash it with deionized water and immerse it in the 1.0 mol/L HCl solution for 20 min. Finally, dry it with nitrogen. In spin coating, the emeraldine base form of PANI powder is synthesized by normal method^[4, 5]. The resulting emeraldine base form is doped with dodecylbenzenesulfonic acid (DBSA) dissolved in CHCl_3 to convert it into the emeraldine salt form, which is the conducting form of PANI. The mole ratio of PANI to DBSA varies between 1: 0.5 and 1: 0.3, and the concentration of PANI/ CHCl_3 was 0.5 wt%. Finally, the resulting PANI(DBSA)/ CHCl_3 solution was used to prepare a thin film on the PS by spin coating.

Metal Electrode

An aluminium electrode coated on the back of PS substrate was evaporated under vacuum, while a gold circular electrode of 3 mm in diameter coated on the PANI film was also evaporated under

vacuum. The copper wires were attached using silver paste.

The I-V characteristics of the heterojunction diode (Al/PS-PANI/Au) were performed at room temperature with ADVANTEST R6142 Programmable DC Voltage/Current Generator and KEITHLEY 196 System DMM. AFM image of PS was recorded by Nano III atomic force microscopy. The room-temperature conductivity of PANI film was measured by four-probe method.

RESULTS AND DISCUSSION

It was found that the rectifying parameters of the heterojunction diode strongly depend on the preparation conditions of PANI and PS, the protonation state and thickness of PANI films, and cell structure as well as the interface between Al electrode and PS. The influences of these factors on the rectifying parameters of heterojunction diode are discussed as follows:

I-V Characteristics of Al/PS-PANI/Au Cell

Typical I-V characteristics of the heterojunction diode are shown in Fig.3. As one can see that the current increases exponentially at a forward applied voltage, but a very small current flows under a reversed applied voltage. This indicates that a rectifying effect of the heterojunction was observed. In general, the physical model for heterojunction diode consists of thermal ion emission, tunneling current, recombination at interface and recombination-tunneling current, which mainly depend on the discontinuity of energy band and interface feature. In fact, the Schottky diode between the semiconductor and the electrode can be considered as an extended heterojunction diode, especially for a semiconductor with high conductivity. In our experiment, the doped PANI itself exhibits metal behavior. Thus, the theory of thermal ion emission may be used to express the I-V characteristic of the heterojunction diode. It was noted that the I-V characteristics of all the heterojunction diodes tested in this paper obey the theory of thermal ion emission^[6], which can be expressed as follows:

$$j = j_0 [\exp(eV / nkT) - 1] \quad (1)$$

$$j_0 = A^* T^2 \exp(-e\phi_b / kT) \quad (2)$$

where V is the applied voltage, T is the temperature, n the ideal factor, k the Boltzmann constant, j_0 the reversed saturated current density. A^* is the Richardson constant taken as $120 \text{ A/cm}^2 \text{ K}^2$ and ϕ_b the barrier height. Thus the rectifying parameters, such as j_0 , n , ϕ_b and rectifying ratio (γ) at given applied field can be obtained from eqs. (1) and (2), respectively.

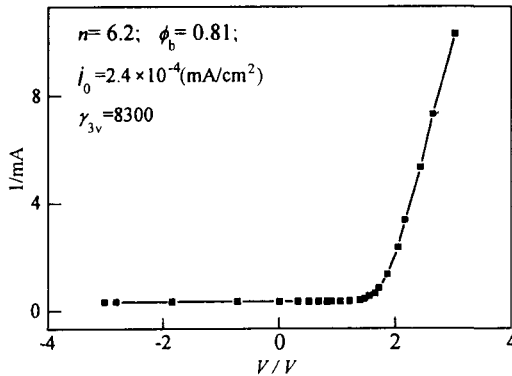


Fig. 3 The I-V characteristic of heterojunction Al/PS-PANI(HCl)/Au cell

Cell Structure and Interface Between Aluminum Electrode and PS

The purpose of this paper is to fabricate a heterojunction diode between PANI and PS. Thus,

ohmic contact between PANI and the electrode or PS and the electrode is required. In the dipping polymerization method, however, the cell structure was Al/PANI-PS-PANI/Au, because a thin PANI film was coated on both the front and the back surfaces of the PS substrate. As a result, the Schottky contact between PANI and Al electrode was formed. In order to fabricate a single p-n junction, the back surface of silicon plate was coated with a black wax before the dipping polymerization of PANI, then it was removed with toluene after the dipping polymerization, followed by the evaporation of the Al electrode under vacuum. With this treatment, a single heterojunction diode between PANI and PS could be fabricated, in which the cell structure is Al/PS-PANI/Au. It was found that a significant difference was observed in the rectifying effect between Al/PANI-PS-PANI/Au and Al/PS-PANI/Au cell as given in Table 1. As one can see, the rectifying parameters of heterojunction diode was improved by eliminating the Schottky contact formed between PANI and the Al electrode. This result suggests that ohmic contact either between a *p*-type semiconductor and a metal electrode, or an *n*-type semiconductor and an electrode, is a very important requirement in fabricating a single heterojunction diode.

Table 1. Effect of cell structure on the rectifying parameters of heterojunction made between PANI and PS

Cell Structure	Dipping time (min)	γ_{3v}	N	ϕ_b (V)	j_0 (mA/cm ²)	j_{3V} (mA/cm ²)
Al/PANI-PS-PANI/Au	14	14	8.5	0.71	8.8×10^{-3}	0.08
	20	130	6.7	0.79	4.7×10^{-4}	3.3
	27	5	11.4	0.83	7.9×10^{-5}	2.6
Al/PS-PANI/Au	14	1300	7.0	0.76	2.2×10^{-2}	130
	20	8300	6.2	0.81	2.4×10^{-4}	143
	27	810	7.4	0.69	1.3×10^{-3}	186

For the dipping polymerization method, the influence of dipping time on the I-V characteristic of the heterojunction diode made between PANI doped with 1.0 mol/L HCl and PS, i.e. Al/PS-PANI(HCl)/Au cell, was observed as shown in Fig.4. Based on the rectifying parameters of the heterojunction diode, the best dipping time for dipping polymerization of PANI was found to be 20 min.

It was found that the interface feature between PS and the Al electrode also affects the rectifying parameters of heterojunction due to the oxidation of PS exposed to air as shown in Fig.5.

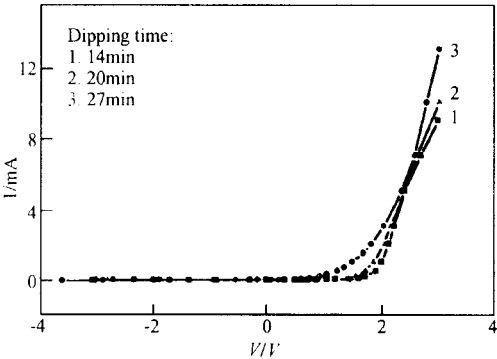


Fig. 4 Effect of dipping time on the I-V characteristic of heterojunction Al/PS-PANI(HCl)/Au cell

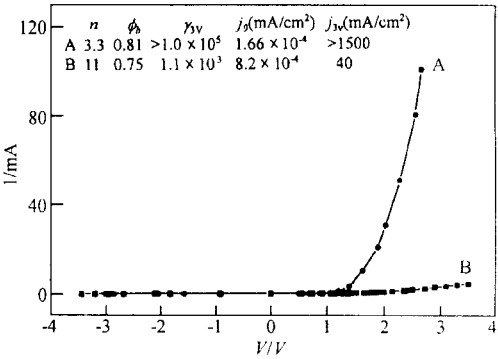


Fig.5 Effect of interface feature between PS and Al electrode on the I-V characteristic of heterojunction Al/PS-PANI(DBSA)/Au cell

It shows that the rectifying effect of heterojunction is significantly improved by a cleaning treatment with a HF solution (40% HF: ethanol = 50:50 / vol.%) for 2 min before the evaporation of Al electrode. The rectifying parameters of this heterojunction diode (curve A in Fig.5) were calculated to be $n = 3.3$, $\phi_b = 0.8$ V, $\gamma > 1.0 \times 10^5$ at 3 V, $j_0 = 1.66 \times 10^{-4}$ mA/cm², and $j > 1500$ mA/cm² at 3 V, respectively. The rectifying factor (γ) of this diode was enhanced by two orders of magnitude as compared with the untreated one. This result indicates that the interface feature either between the p - n junction or between the semiconductor and the metal electrode is an important factor to control the rectifying characteristic of the heterojunction diode.

The Protonation State and Thickness of PANI Films

In order to investigate the effect of the protonation state and thickness of the PANI film on the I-V characteristic of the heterojunction diode, DBSA was used as dopant, and the mole ratio of PANI to DBSA varied between 1:0.3 and 1:0.5. A thin PANI film was coated on the PS substrate by spin coating with PANI(DBSA)/CHCl₃ solution for the given concentration, and the thickness of PANI film was controlled by spin numbers at the given spin speed, and was estimated to be 0.1 μ m ~ 0.3 μ m by SEM method. The protonation state of PANI strongly affect the rectifying effect of heterojunction as shown in Fig.6, and the corresponding rectifying parameters are given in Table 2.

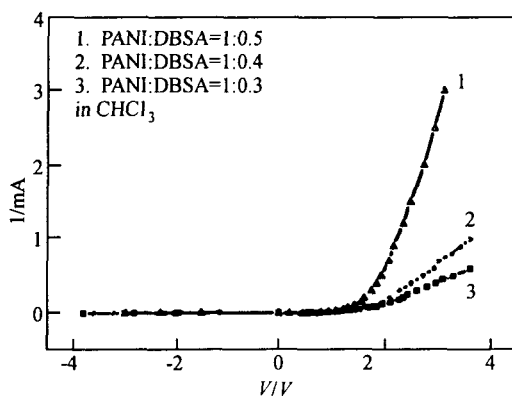


Fig.6 Effect of the protonation state of PANI on the I-V characteristic of heterojunction Al/PS-PANI(DBSA)/Au cell

It is evident that the higher the protonation state of PANI, the higher the rectifying ratio, the current density and the reversed saturated current density. This is consistent with the fact that the conductivity of PANI at room temperature is enhanced by increasing the protonation state^[7,8]. On the other hand, the ideal factor (n) and barrier height (ϕ_b) of the heterojunction diode are almost independent of the protonation state within experimental error, for example, $\phi_b = 0.74 \sim 0.76$ V, and $n = 7.3 \sim 8.2$ were found. This indicates that the work function of doped PANI with DBSA could not be adjusted by changing the protonation state, as the mole ratio of PANI to DBSA varied between 1:0.3 and 1:0.5. This is consistent with the results that the room-temperature conductivity of PANI is almost independent of the protonation state when it reaches the metallic region^[7,8]. The influence of the thickness of the PANI films over the rectifying parameters of the heterojunction is observable from Table 3. Most of the rectifying parameters, such as j_0 , γ at 3 V, and output current are improved by reducing the thickness of the PANI film. However, ϕ_b varied between 0.75 V and 0.77 V, which is independent of the thickness of PANI film, and is also in agreement with the results obtained from the experiment on the protonation state of PANI (see Table 2).

Table 2. Effect of the protonation state of PANI on the rectifying parameters of heterojunction of Al/PS-PANI(DBSA)/Au cell

No.	PANI:DBSA	ϕ_b (V)	N	γ_{3v}	j_0 (mA/cm ²)	j_{3v} (mA/cm ²)
1	1 : 0.5	0.74	8.2	2900	3.3×10^{-3}	40
2	1 : 0.4	0.76	8.0	350	1.0×10^{-3}	10
3	1 : 0.3	0.76	7.3	208	1.5×10^{-3}	6.1

Table 3. Effect of the thickness of PANI film on the rectifying parameters of heterojunction of Al/PS-PANI(DBSA)/Au cell

No.	Coating layers	ϕ_b (V)	N	γ_{3v}	j_0 (mA/cm ²)	j_{3v} (mA/cm ²)
1	1	0.75	11.0	1100	1.8×10^{-3}	40
2	3	0.77	8.0	250	4.9×10^{-3}	26
3	5	0.77	7.3	50	8.7×10^{-3}	21

Porous Silicon Layer and Metal Electrode

To examine the effect of preparation condition of porous silicon layer, the PANI film coated on the PS substrate was fabricated by dipping polymerization, in which 0.15 mol/L aniline monomer and 0.075 mol/L ammonium persulfate as oxidant was used and the dipping polymerization time was 27 min. The PS layer was anodized electrochemically in the HF solution (40% HF: ethanol = 50:50 / vol.%) at an applied voltage of 10V, 15V and 25 V for 10 min. It was found that the higher the anodic voltage, the higher the output current, the higher the rectifying ratio, and the lower the reversed saturated current density, as shown in Fig. 7. However, the ideal factor ($n = 5.2\sim 5.9$) and barrier height ($\phi_b = 0.67 \sim 0.68V$) are not affected by the anodized voltage of PS. Moreover, it is very interesting to find that the rectifying feature of heterojunction diode was improved by increasing the thickness of the Au electrode, due to an island morphology of the thinner film (see Fig.8).

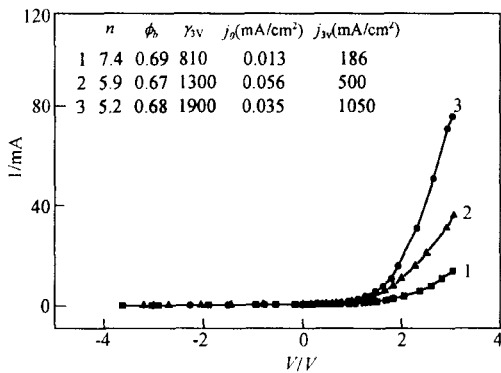


Fig. 7 Effect of the anodized voltage of PS on the I-V characteristic of heterojunction Al/PS-PANI(HCl)/Au cell
1. 10 V, 2. 15 V, 3. 25V anodized for 10 min

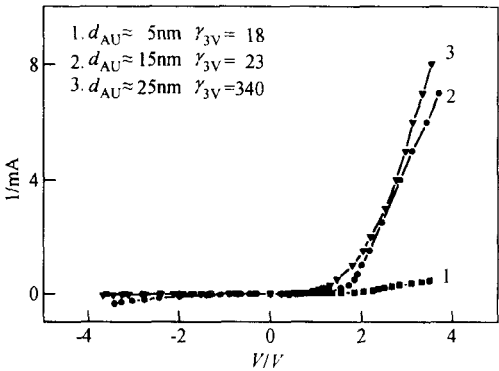


Fig.8 Effect of the thickness of Au electrode on the I-V characteristic of heterojunction Al/PS-PANI(DBSA)/Au cell

CONCLUSIONS

The rectifying heterojunction diode made between PANI and PS was fabricated, and the rectifying characteristics were measured as a function of the preparation conditions of PANI and PS, the protonation state and thickness of PANI, as well as cell structure and interface between PS and the

Al electrode. The main results obtained in this paper are summarized as follows: 1. The rectifying heterojunction diode made between PANI and PS was fabricated as follows: the PANI film was prepared by dipping polymerization and spin coating, and PS was prepared by electrochemical anodization. The I-V characteristic of the heterojunction diode can be expressed by the theory of thermal ion emission. 2. The rectifying parameters of the heterojunction diode were measured as $\phi_b = 0.67 \sim 0.83$ V for the barrier height between PANI and PS, $n = 3 \sim 12$ for the ideal factor, $\gamma = 1.8 \times 10^1 \sim 1.0 \times 10^5$ for the rectifying ratio at 3V, and $j_0 = 8.0 \times 10^{-5} \sim 5.6 \times 10^{-2}$ mA/cm² for the reversed saturated current density, respectively. The rectifying parameters of PANI-PS heterojunction diode, such as γ , n , ϕ_b , j_0 , strongly depend on the preparation conditions of PANI and PS, the protonation state and thickness of PANI, and cell structure. 3. The rectifying effect of the heterojunction diode can be improved by preventing the oxidation of PS before evaporating the Al electrode under vacuum. In this way, heterojunction diode with higher rectifying factor ($\gamma > 1.0 \times 10^5$ at 3V), higher output current (> 1500 mA/cm² at 3V) and lower ideal factor ($n = 3.3$) can be obtained.

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