

## HETEROJUNCTION DIODES OF POROUS SILICON WITH SOLUBLE POLYANILINE\*

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**Abstract** Two kinds of heterojunction diodes of porous silicon (PS) with soluble polyaniline (PANI) were fabricated. One is a heterojunction diode of PS with water-soluble copolymer of polyaniline (PAOABSA), Al/PS-PAOABSA/Au cell as rectifying diode. Another is a heterojunction diode of PS with soluble polyaniline doped with DBSA, Al/PS-PANI (DBSA)/Au cell as light emitting diode (LED). The rectifying characteristics of the rectifying diodes were measured as a function of the degree of sulfonation and thickness of the copolymers, as well as oxidation of PS. The rectifying ratio of the heterojunction can reach  $5.0 \times 10^4$  at  $\pm 3$  V bias. For the LED, the photoluminescence (PL) and electroluminescence (EL) spectra were measured and discussed.

**Keyword** Heterojunction diodes, Porous silicon, Polyaniline, LED

### INTRODUCTION

Since conjugated polymer light-emitting diodes (LED) were first reported in 1990 using poly(phenylene vinylene) (PPV) as light emitting materials<sup>[1]</sup>, the application of conducting polymers in LED has attracted much attention because polymer semiconducting materials possess many advantages over inorganic semiconducting materials, such as low cost, simple process, light weight and variable emitting color. Up till now, PPV and its derivatives remain the most popular polymers in fabricating LED devices. Recently, however, the application of polyaniline (PANI) as typical conducting polymers in LED devices has been reported in the literature<sup>[2-4]</sup>. Gustafsson *et al.*<sup>[2]</sup> reported that soluble PANI as the hole-injecting electrode was used in the LED with PPV as the electroluminescent layer. Wang *et al.*<sup>[3]</sup> reported that the emeraldine base form of PANI as insulating layer between the emissive polymer layer of poly(2,5-dihexadecanoxo phenylene vinylene pyridyl vinylene) (PPV-PPyV) and the electrode could improve the characteristics of the devices. In particular, Chen *et al.*<sup>[4]</sup> reported that nearly white light covering the full range of visible light (380~750) can be emitted from LED devices with an emeraldine base form of PANI as the light emitting material. These results indicated that PANI has an important role in LED devices.

At the same time, the discovery of visible luminescence from porous silicon (PS) has stimulated great interest in this material because of the possibility of fabricating silicon wafers and incorporating microelectronic devices using existing technologies<sup>[5]</sup>. Thus, it is expected that a heterojunction of PS with conducting polymers might open a new way to fabricate new types LEDs. In fact, some papers covering heterojunction devices of PS with conducting polymers have

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been published in the literature. For instance, Halliday *et al.*<sup>[6]</sup> reported that a heterojunction between PS and the doped polyaniline with camphor sulfonic acid (PANI-CSA) exhibited a very broad electroluminescence (EL) band from 500 to 1000 nm with a peak at 790 nm. Bisey *et al.*<sup>[7]</sup> also observed a similar phenomenon. In our laboratory, the rectifying ratio of Al/PS-PANI(HCl)/Au heterojunction diode reached  $10^5$  at 3 V bias<sup>[8]</sup>, which is much higher than that of Halliday's results in which the rectifying ratio is 490 at 5 V bias<sup>[6]</sup>. Moreover, PS heterojunctions with polythiophene (PTH)<sup>[9]</sup> and polypyrrole<sup>[10]</sup> have also been reported.

In addition, it is expected that water-soluble conducting polymers are good candidates for fabricating such electronic devices because water is the cheapest solvent which does not cause environmental pollution. The first protonic acid self-doped polyaniline (SPAN) with room-temperature conductivity of 0.1 S/cm was reported by Yue *et al.*<sup>[11]</sup>. The degree of sulfonation of SPAN, defined as the sulfur to nitrogen (S/N) ratio was 0.5 and cannot be changed. The electroluminescence properties of LED consisting of a SPAN/PPV multilayer thin film as emitting material were reported by Onoda *et al.*<sup>[12–13]</sup>. In our laboratory, poly(aniline-*co*-aminobenzenesulfonic acid) (PAOABSA) was successfully synthesized by a one-step chemical polymerization<sup>[14]</sup>. Compared to SPAN, the copolymer of PAOABSA shows high room-temperature conductivity (3.4 S/cm) with adjustable degrees of sulfonation ( $F_1 = 0.15\sim0.34$ ). It has been also found that the conductivity and solubility of the copolymer in aqueous solution strongly depend on the degree of sulfonation, and a thin film of PAOABSA copolymer can be made by the spin coating method. Thus, it is expected that the copolymer of PAOABSA is a good candidate for the fabrication of heterojunction devices with PS.

In this article, water-soluble PAOABSA copolymers were used to fabricate heterojunction devices with PS as rectifying diode and the rectifying characteristics of the heterojunction devices, Al/PS-PAOABSA/Au cells, were measured as a function of the degree of sulfonation and the thickness of the copolymer as well as the oxidation of silicon. Moreover, heterojunction devices of PS with doped PANI, Al/PS-PANI(DBSA)/Au cells, as LED devices are discussed based on photoluminescence (PL) and electroluminescence (EL) spectra.

## EXPERIMENTAL

PS films were obtained by the electrochemical anodization process<sup>[15]</sup> using *n*-type silicon ( $\langle 100 \rangle$ ,  $6\times 11\text{ mm}^2$ , 0.51 mm thick,  $\rho$  from 3 to 5). A typical process for PS preparation was described as follows: A Si substrate was cleaned ultrasonically using isopropyl alcohol for 10 min and then washed with  $\text{H}_2\text{O}_2$  solution to remove the organic and inorganic materials stuck to the surface of the Si substrate. Consequently, a layer of black paste covered the back of the silicon substrate. Then the resulting Si substrate was electrochemically anodized under a constant current density of  $0.3\text{ mA cm}^{-2}$ , in a HF-ethanol solution (50:50 vol%) for 10 min and then rinsed with deionized water and dried in argon. Finally, the layer of black paste was removed using toluene.

The emeraldine base form of polyaniline was synthesized using a standard method<sup>[16]</sup> and then dissolved in  $\text{CHCl}_3$  solution containing an excess of DBSA to obtain an emeraldine salt of PANI (PANI-DBSA). The copolymer of PAOABSA was synthesized by chemical polymerization of aniline and *o*-aminobenzenesulfonic acid in an aqueous solution of 1.2 mol/L HCl with ammonium persulfate as oxidant. The synthetic procedure has been described in detail in [14]. By this method, copolymers with various degrees of sulfonation ( $F_1 = 0.15\sim0.34$ ) were synthesized. They were then dissolved in 1 mol/L  $\text{NH}_3$  solution with a concentration of 1.0 wt%. The resulting PAOABSA solutions were deposited on porous silicon films using the spin-coating method. The aluminum electrode was evaporated on the back of the PS substrate to produce an Ohmic contact and the gold electrode was evaporated onto the PAOABSA film. Finally, copper wires were attached using silver paste to obtain the heterojunction Al/PS-PAOABSA/Au cell. The Al/PS-PANI(DBSA)/Au

cell was fabricated in the same way. Schematic structure of heterojunction devices of PS with PANI and its copolymer is shown in Fig. 1.

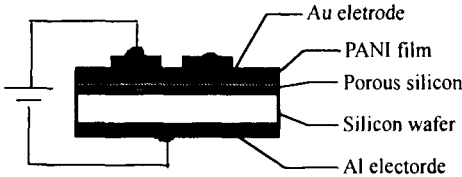


Fig. 1 The schematic structure of heterojunction devices of PS with PANI and its copolymers

I-V curves of the heterojunction diodes were obtained at room temperature using ADVANTEST R6142 programmable DC voltage / current generator as constant current source and Keithley 196 system DMM. The thickness of the copolymer was measured by the SEM method (S-530). X-ray photoelectron spectroscopy (XPS) analyses were carried out using ES-300 (Kratos). The conductivity at room temperature was measured by the four-probe method. The PL and EL spectra of Al/PS-PANI(DBSA)/Au cell were measured by Renishaw 1000.

RESULTS AND DISCUSSION

Heterojunction of PS with PAOABSA Copolymer as Rectifying Device

The I-V characteristic curves of the heterojunction, Al/PS-PAOABSA/Au cell, with different degrees of sulfonation of PAOABSA are shown in Fig. 2. The rectifying ratio ( $\gamma$ ) can be obtained from the ratio of forward current to reverse current at specific bias. For instance, the forward current for PAOABSA ( $F_1 = 0.15$ , in Fig. 1a) is 1100  $\mu\text{A}$  and the reverse current is measured and found to be  $-1.8 \mu\text{A}$ . Then the  $\gamma$  (at  $\pm 3 \text{ V}$ ) is calculated to be 6000. The I-V characteristics can be fitted to the thermoionic emission theory<sup>[17, 18]</sup> expressed by:

$$J = J_0 [\exp(eV/nkT) - 1]$$
 (1)

where  $V$  is the applied bias,  $n$  is the ideality factor,  $k$  is the Boltzmann constant and  $J_0$  is the reverse saturated current density. At room temperature, because  $eV \gg nkT$ , Eq. (1) can be rewritten as:

$$J = J_0 \exp(eV/nkT)$$
 (2)

and  $J_0$  is given by:

$$J_0 = A^* T^2 \exp(-e\phi_b/kT)$$
 (3)

where  $A^*$  is the Richardson constant and  $\phi_b$  is the barrier height.

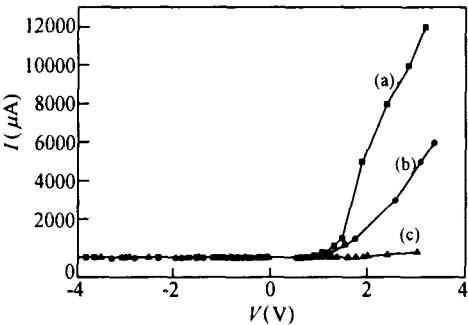


Fig. 2 I-V characteristics of the heterojunction between PS and PAOABSA with different degrees of sulfonation  
a)  $F_1 = 0.15$ , b)  $F_1 = 0.30$ , c)  $F_1 = 0.34$

Fitting  $\ln J$  versus  $V$  at low forward biases, the ideality factor  $n$  and reverse saturated current

density  $J_0$  can be calculated. Based on eq. (3) the barrier height  $\phi_b$  can be calculated if  $A^*$  was taken as  $120 \text{ A} \cdot \text{cm}^{-2} \text{ K}^{-2}$ . These physical parameters are given in Table 1. Firstly, the rectifying ratio at given bias (e.g. at 3 bias) decreases with the increase of the degree of sulfonation ( $F_1$ ) of the PAOABSA copolymers. This is consistent with our previous results that the conductivity of copolymers at room temperature decreases with an increase of the degree of sulfonation<sup>[14]</sup>. This may be attributed to the lower electron density in the backbone of the copolymer due to the electron-withdrawing capability of the  $\text{SO}_3^-$  group attached directly to the benzene ring. Moreover, the steric effects of *o*-aminobenzenesulfonic acid substituents produce torsional twists and shorten the conjugation lengths in the polymer as is proved by the UV-Vis spectra. This may be another reason for the decrease of room-temperature conductivity and the reduction of rectifying ratio with increasing degree of sulfonation. Secondly, the ideality factor ( $n$ ) of the heterojunction diode increases from 5.1 to 10.4 when the degree of sulfonation increases from 0.15 to 0.34. This shows that a longer conjugated  $\pi$  electron and a larger electronic density are favorable for high room-temperature conductivity and rectifying behavior of the Al/PS-PAOABSA/Au heterojunction. Thirdly, the barrier height ( $\phi_b$ ) increases from 0.48 V to 0.52 V with increasing sulfonation of the PAOABSA copolymer. This suggests that the work function of PAOABSA can be adjusted by changing the degree of sulfonation. As described above, a lower degree of sulfonation of PAOABSA favors an excellent rectifying effect of the Al/PS-PAOABSA/Au heterojunction.

**Table 1** The rectifying parameters of PS-PAOABSA heterojunction with different degrees of sulfonation of the PAOABSA copolymers

| Degrees of sulfonation ( $F_1$ ) | $\gamma$ (at $\pm 3\text{V}$ ) | $n$  | $J_0$ ( $\text{mA}/\text{cm}^2$ ) | $\phi_b$ (V) |
|----------------------------------|--------------------------------|------|-----------------------------------|--------------|
| 0.15                             | 6000                           | 5.08 | $3.4 \times 10^{-4}$              | 0.48         |
| 0.30                             | 86                             | 8.30 | $1.6 \times 10^{-4}$              | 0.50         |
| 0.34                             | 60                             | 10.4 | $8.0 \times 10^{-5}$              | 0.52         |

The PAOABSA copolymer with a degree of sulfonation of 0.3 was used to study the influence of the thickness of the PAOABSA copolymer on the rectifying characteristic of the heterojunction. The thickness of the PAOABSA copolymer was controlled by spin-coating different numbers of layers of the copolymer. This was measured by SEM. The related rectifying parameters of PS-PAOABSA heterojunction with different film thicknesses of the copolymer are given in Table 2. It can be seen that the rectifying characteristic of the heterojunction device was improved when the film of the copolymer became thinner. For example, the rectifying ratio at 3 V bias was enhanced by two orders of magnitude when the thickness of the copolymer film decreased from 5  $\mu\text{m}$  to 1  $\mu\text{m}$ . From the experimental results, it is evident that the thinner film of PAOABSA without pin-hole favors the ideal rectifying effect.

**Table 2** The rectifying parameters of PS-PAOABSA heterojunction with various thicknesses of PAOABSA film

| Thickness ( $\mu\text{m}$ ) | $\gamma$ (at 3 V) | $n$ | $J_0$ ( $\text{mA}/\text{cm}^2$ ) | $\phi_b$ (V) |
|-----------------------------|-------------------|-----|-----------------------------------|--------------|
| 5                           | 86                | 8.3 | $1.6 \times 10^{-4}$              | 0.50         |
| 3                           | 333               | 3.3 | $3.8 \times 10^{-5}$              | 0.54         |
| 1                           | 4100              | 3.3 | $6.0 \times 10^{-6}$              | 0.58         |

It was known that the interface is an important factor for the rectifying effect of the Schottky or heterojunction diodes. There exist three interfaces of Al/PS, PS/PAOABSA and PAOABSA/Au in Al/PS-PAOABSA/Au cells. For the interface of PS/PAOABSA, its oxidation has been studied in another paper<sup>[19]</sup>. Since the Au electrode is very stable to oxygen, it does not oxidize easily. Therefore, in this paper, the oxidation of Al/PS interface is discussed. In order to examine the influence of the interface between the Al electrode and porous silicon on the rectifying effect of the

heterojunction diode, the fabrication process of the heterojunction device was modified as follows: After the Si substrate was cleaned ultrasonically using isopropyl alcohol for 10 min, it was washed with  $\text{H}_2\text{O}_2$  solution and rinsed using deionized water and dried in argon. The Al electrode was evaporated immediately. A layer of black paste covered the Al film and the Si substrate was oxidized by electrochemical anodization to form a porous Si film. Then a PAOABSA film was deposited on the PS film and the layer of black paste on the Al film was removed using toluene. Finally, the Au electrode was evaporated on the PAOABSA film and copper wires were linked using silver paste on the Al electrode. For the PAOABSA film with a specific degree of sulfonation (i.e.  $F_1 = 0.30$ ) and a specific thickness (such as  $1\ \mu\text{m}$ ), the rectification ratio increased from  $4.1 \times 10^3$  for the previously stated process to  $5.0 \times 10^4$  for the improved process. Based on the XPS analysis of the surface of the Si substrates for the two processes as shown in Fig. 3, it was found that the binding energy of the  $\text{Si}_{2p}$  for the improved method is 99.27 eV, close to the binding energy of a single crystal of Si (99.15 eV). However, the  $\text{Si}_{2p}$  spectrum for the previous process can be resolved into three peaks: at 99.09 eV (80.91 %) corresponding to the Si single crystal, at 100.96 eV (7.77%) and at 102.11 eV (11.32%) which is close to that of the  $\text{SiO}_2$ . This indicates that there was a small amount of oxygen on the Si surface for the previous process. Therefore, the results obtained from XPS measurements indicate that the oxidation of silicon is harmful for the rectifying devices, and the technique of fabricating process is very important for an excellent rectifying device of the heterojunction between PS and PAOABSA copolymer.

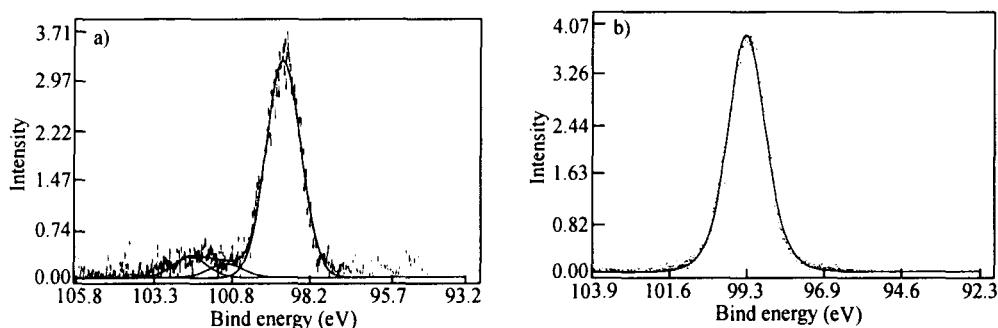


Fig. 3 The XPS spectra of  $\text{Si}_{2p}$  element for the Si substrate  
a) the previous process, b) the improved process

### Heterojunction Devices of PS with Doped PANI as LED

The above rectification diodes were further used as LED. But no EL phenomenon was observed when forward bias voltage was applied. On the other hand, the heterojunction between soluble PANI and porous silicon, Al/PS-PANI(DBSA)/Au cell, has excellent rectifying effect<sup>[20]</sup>. The rectifying ratio of the heterojunction diode can reach  $10^5$  at  $\pm 3$  V. Therefore, soluble PANI was used to fabricate heterojunction LED with porous silicon. An argon laser emitting at 488 nm was used as the light source because PANI provides a transmission window<sup>[21]</sup>. The PL spectrum of the heterojunction diode is shown in Fig. 4. Comparing with the PL spectrum of Al/PS/Au cell, which shows red PL centered at 700 nm, the PL spectrum of Al/PS-PANI (DBSA)/Au cell shifted to blue, centered at 660 nm. The shift behavior is probably due to the light absorption of the emitted light into the PANI layer. Moreover, the intensity of the PANI covered PS film is stronger than that of the bare PS film, which is different from Bsieys's<sup>[7]</sup> but similar to that by Parkhutik<sup>[22]</sup>. When the device was forward biased (positive applied to the polyaniline) to about 10~15 V, the Al/PS-PANI (DBSA)/Au cell emitted visible light (500~900 nm) (shown in Fig. 5). However, for the Al/PS/Au cell, visible light (500~1000 nm) was observed when the forward voltage was up to 30 V. Furthermore, it can be seen from Fig. 5 that the emission band for the EL of Al/PS-PANI (DBSA)/Au cell shifted from 660 nm to 680 nm when compared with the PL spectrum in Fig. 4. In other words, the

peak shifted much further into the infrared region. This is consistent with previous reports<sup>[6, 7]</sup>. Therefore, it is clear that the drive voltage can be decreased when the PANI film is coated on PS. This indicates that PANI makes electrical contact with a significant fraction of the porous silicon layer. Halliday *et al.*<sup>[6]</sup> suggested that the electroluminescence originates from electron-hole recombination in the porous silicon wires. The holes will be injected into the porous silicon valence band from the hole-type polaron band in the polyaniline through a very thin silicon oxide layer. The electrons will be injected from the silicon wafer into the porous silicon conduction band.

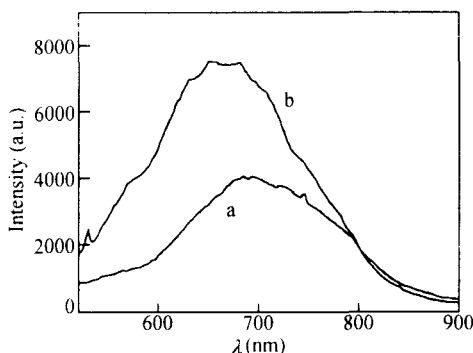


**Fig. 4** The PL spectra of PANI-PS heterojunction diode  
a) pure PS film; b) PS covered with PANI film

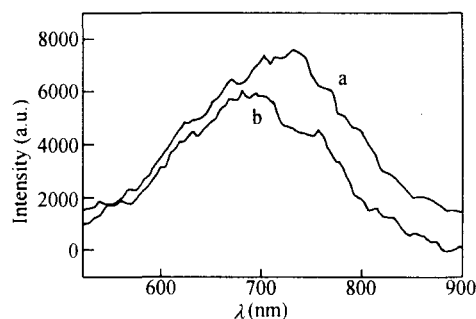


**Fig. 5** The EL spectra of PANI(DBSA)-PS heterojunction diode  
a) pure PS film; b) PS covered with PANI film

## CONCLUSIONS

Heterojunction devices of PS with water-soluble copolymer of polyaniline (PAOABSA), Al/PS-PAOABSA/Au cell as rectifying diodes, were fabricated. It was found that decreasing degrees of sulfonation and thickness of the copolymer as well as oxidation of PS improves the rectifying characteristics. Moreover, heterojunction devices of PS with soluble polyaniline doped with DBSA, Al/PS-PANI (DBSA)/Au cell as LED with visible light (500~900 nm), were fabricated. Compared to Al/PS/Au LED, a coating of PANI film onto PS not only decreases the drive voltage of LED, but also changes the PL and EL spectra of Al/PS/Au cell LED.

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