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Rectifying effect of heterojunctions between metals and doped conducting polymer nanostructure pellets*

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This paper reports that the Schottky junctions between low work function metals (e.g. Al and In) and doped semiconducting polymer pellets (e.g. polyaniline (PANI) microsphere pellet and polypyrrole (PPy) nanotube pellet) have been prepared and studied. Since Ag is a high work function metal which can make an ohmic contact with polymer, silver paste was used to fabricate the electrodes. The Al/PANI/Ag heterojunction shows an obvious rectifying effect as shown in $I-V$ characteristic curves (rectifying ratio $\gamma = 5$ at ± 6 V bias at room temperature). As compared to the Al/PANI/Ag, the heterojunction between In and PANI (In/PANI/Ag) exhibits a lower rectifying ratio $\gamma = 1.6$ at ± 2 V bias at room temperature. In addition, rectifying effect was also observed in the heterojunctions Al/PPy/Ag ($\gamma = 3.2$ at ± 1.6 V bias) and In/PPy/Ag ($\gamma = 1.2$ at ± 3.0 V bias). The results were discussed in terms of thermoionic emission theory.

Keywords: Schottky junctions, rectifying effect, conducting polymer nanostructures
PACC: 7340S, 7340E, 7340C, 6146

1. Introduction

In general, electrical conductivity of conducting polymers can cover a wide range from $10^{-10} - 10^{4}$ S/cm through doping. Recently, conducting polymers have attracted considerable attention in the fabrication of electronic devices based on metal-semiconductors (i.e. Schottky diodes) or p-n diodes. A series of papers concerning above devices with conducting polymers have been published.[1−4] For example, Na-doped polyacetylene and AsF_5-doped polyacetylene form a p-n junction and show typical rectifying characteristics.[3] Moreover, heterojunctions between conducting polymers and inorganic semiconductor, such as p-doped polyacetylene / CdS or n-ZnS, were also reported to show rectifying characteristics of p-n junction.[4] However, heterojunctions made between conducting polymer nanostructures and metals have not been reported intensively yet.

In recent years, conducting polymer nanostructures have attracted considerable attention due to their unusual properties and potential applications in nano-electronics. By now there are many methods to synthesize polymer nanostructures, such as template synthesis, electrospinning and template-free method etc. More details can be found in Ref.[5]. In this article, semiconducting polyaniline (PANI) microspheres and polypyrrole (PPy) nanotubes were prepared by template-free method, because PANI and PPy are two of the most attracting conducting polymers due to relatively high conductivity and good stability in air.

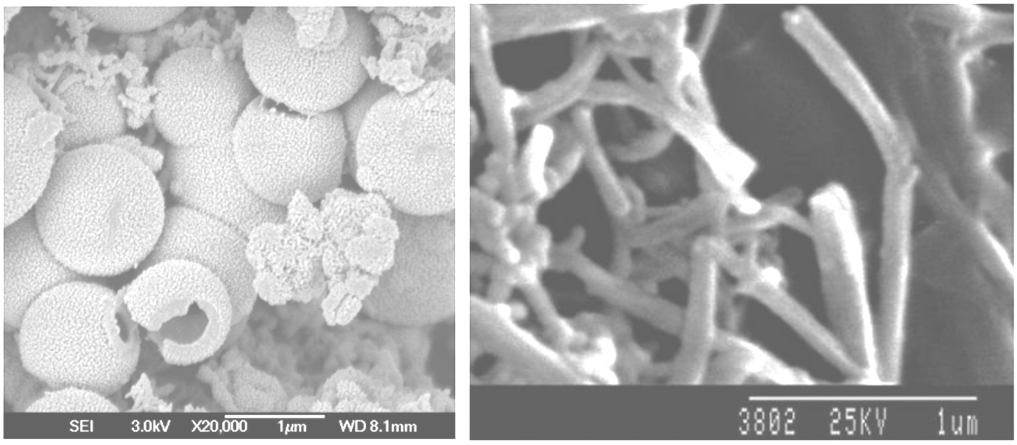
Here, heterojunction between doped PANI microsphere pellet and Al was fabricated, the rectifying characteristics were measured at room temperatures and 267 K, and the effect of temperature on the rectifying feature was discussed. The Schottky diodes fabricated by In/PANI/Ag, Al/PPy/Ag, and In/PPy/Ag were also measured and discussed in comparison with the heterojunction Al/PANI/Ag.

2. Experimental

$\beta-$naphthalene sulfonic acid (NSA) doped hollow PANI microspheres and PPy nanotubes were synthesized by a self-assembly method.[6] Aniline monomer

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and pyrrole monomer were distilled under reduced pressure. Ammonium persulfate (APS), NSA, and other reagents were used as received without further treatment. In a typical synthesis procedure, aniline and NSA with molar ratio of 2:1 were dissolved in distilled water at room temperature by ultrasonic stirring for 10 minutes, and an aqueous solution of APS (molar ratio APS/aniline = 1 : 1) was added. Then, the mixture was cooled to −10°C quickly and maintained there for 48 h (if the mixture is cooled to 0°C in an ice bath, PANI-NSA nanotubes will be obtained). The resulting dark green PANI-NSA precipitate was filtered, and washed with distilled water, alcohol, and ether several times to remove impurities, and was finally dried in a dynamic vacuum at room temperature over 24 h. NSA doped PPy nanotubes can be prepared by carrying out a similar route. The morphologies and structures of the resulting polymer nanostructures have been characterized. Figure 1 shows typical scanning electron microscope (SEM) images of the PANI microspheres and PPy nanotubes. More details can be found in Refs.[6–8].



(a) (b)

Fig.1. Typical SEM images of (a) PANI microspheres and (b) PPy nanotubes.

The dried PANI and PPy powders were pressed into pellets by hydraulic press (∼ 5 MPa) with a thickness about 0.3 mm. Here we note that the tubular and spherical structures can not be observed by SEM either in the surface or the cross section of the pellets due to the pressure used in the compaction step. The heterojunctions Al/polymer/Ag and In/polymer/Ag are fabricated and shown in Fig.2. Al (In) film was made by vacuum evaporation and the property of conducting polymer will not be destroyed in this process. The electrodes were expediently fabricated with silver paste which has a high conductance and forms an ohmic contact with conducting polymers to connect sample and copper wires. The electrical transport properties of the heterojunctions were measured by using Keithley 220 programmable current source and 181 nanovoltmeter between electrodes A and B, or electrodes A and C.

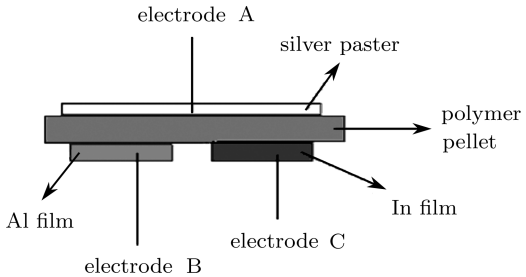


Fig.2. The schematic diagram of heterojunction diodes made between Al (In) and polymer pellet.

3. Results and discussion

The heterojunction of Al/PANI/Ag was measured at room temperature and the $I-V$ characters of device are showed in Fig.3(a). The diode exhibits rectifying effect (the rectifying ratio $\gamma = 5$ at ± 6 V bias) and shows a nonlinear and asymmetric feature in the $I-V$ characteristic curve. As compared to the diode Al/PANI/Ag, the rectifying effect of diode In/PANI/Ag is shown in Fig.3(b), the rectifying ra-

tio is $\gamma = 2.5$ at $\pm 2\,\mathrm{V}$ bias. It is seen that the metal Al makes a higher rectifying contact with PANI than the metal In. PANI, which is a p-type semiconductor, and the metals having a work function lower than that of PANI ($\Phi_\mathrm{m} < \Phi_\mathrm{s}$) make a Schottky barrier. Al has a lower work function ($\Phi_\mathrm{Al} = 3.74\,\mathrm{eV}$) than that of In ($\Phi_\mathrm{In} = 4.12\,\mathrm{eV}$), so, the barrier height may be one of factors affecting the rectifying effect. Here it should be noted that the $I-V$ characteristics of metals/polymer Schottky diode are not exactly the same as those of metal/inorganic semiconductor junctions, owing to the fact that the structure of polymeric semiconductors is highly defected and noncrystalline.[8]

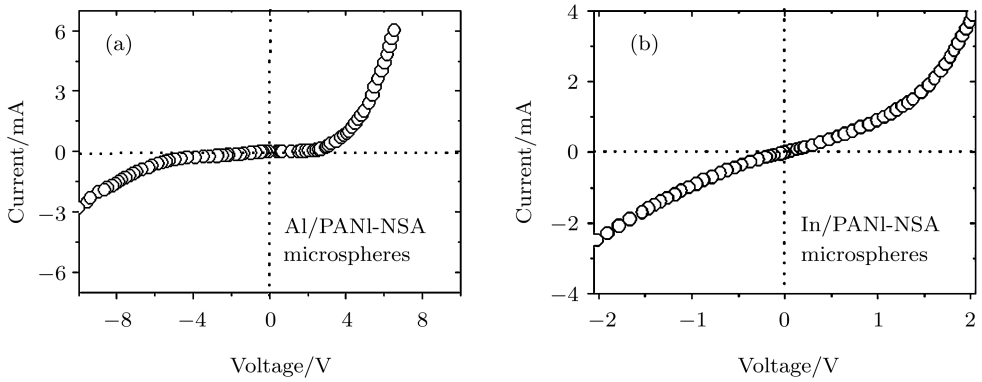


Fig.3. $I-V$ characteristic of heterojunction diodes at room temperature (a) Al/PANI/Ag, (b) In/PANI/Ag.

$I-V$ characteristics of the metal/polymer diodes can be described by the thermoionic emission theory[9] as:

$$I = I_0 \exp[qV/(nkT)]. \tag{1}$$

In Eq.(1) I_0 is the reverse saturation current

$$I_0 = AA^*T^2 \exp[-q\Phi_\mathrm{b}/(kT)], \tag{2}$$

where A^* is the Richardson constant, I is the applied current, q is the electron charge ($1.6 \times 10^{-19}\,\mathrm{C}$), T is the absolute temperature, k is the Boltzmann constant ($1.38 \times 10^{-23}\,\mathrm{J/K}$), n is the ideality factor of Schottky barrier diode, Φ_b is the barrier height of Schottky diodes, A is the effectual area at the interface between Al (In) and PANI. Thus, I_0 and n parameters can be calculated from the slope and intercept of the straight line of $\ln I$ versus V at lower applied voltages. The barrier height (Φ_b) also can be estimated by Eq.(2) if taking A^* as $120\,\mathrm{A}\cdot\mathrm{cm}^{-2}\cdot\mathrm{K}^{-2}$.[10] The data fitting was actualized to the rectifying characteristic of Al/PANI/Ag diode as shown in Fig.4. It is apparent that thermoionic emission theory can fit the data very well. Here we note that the ideality factor $n = 1$ for an ideal diode. However, n usually has a value greater than 1. High values of n can be attributed to the presence of the interfacial thin native oxide layer, series resistance etc. From Table 1, we can see that Al makes a lower ideality factor n and reverse saturation current I_0 with PANI than In. So, we conclude that Al/PANI/Ag junctions can make a better rectifying effect with a higher rectifying ratio than In/PANI/Ag junctions, which is consistent with previous reported results.[8]

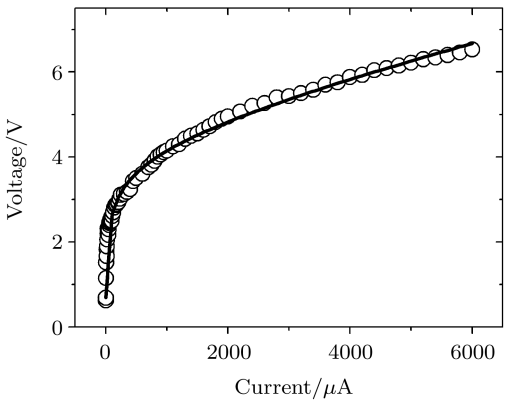


Fig.4. The fitting data curve of Al/PANI-NSA/Ag diode at room temperature.

Table 1. Fitting parameters of Al/PANI/Ag diode at room temperature.

metal	I_0/A	n
Al	7.338×10^{-7}	20.75832
In	0.0004	31.14963

By now, only few papers dealing with rectifying effect at low temperature have been reported. In this article, the heterojunction diode of Al/PANI/Ag was

also measured at $T = 267\,\mathrm{K}$. The $I - V$ characteristic curve is showed in Fig.5. It is apparent that the rectifying effect declines ($\gamma = 2.5$ at $\pm 2\,\mathrm{V}$ bias) with

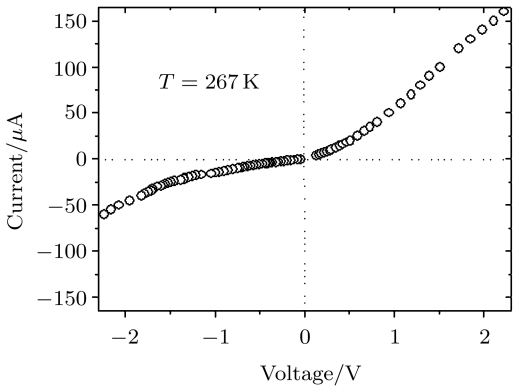


Fig.5. $I - V$ characteristic of diode Al/PANI/Ag at $T = 267\,\mathrm{K}$.

the decrease of temperature. So, temperature is another possible factor that can affect the rectifying effect. It is well known that the $I - V$ characteristics of conducting polymer/semiconductor structures are dependent on temperature, as same as Schottky diodes.[11] In many experimental studies, in which $I-V$ plots are measured as a function of temperature, it is usually observed that the measured $I - V$ Schottky barrier height depends on the temperature. This is usually explained in terms of the weak temperature dependence of the semiconductor band gap. Besides, the series resistance is an important parameter on the electrical characteristics of the rectifying contacts or junctions.[12] For the present case, we propose that the rectifying ratio decreases a little at 267 K because the fact that the resistance of PANI pellets increases exponentially with lowering temperature.[13]

In addition, the heterojunction diodes of Al/PPy/Ag and In/PPy/Ag were also fabricated and their $I - V$ characteristics were measured as showed in Fig.6 The same as junction of Al(In)/PANI/Ag, apparently, the metals Al and In make a rectifying contact with the PPy-NSA. The rectifying ratio of Al/PPy/Ag junction can be calculated $\gamma = 3.2$ at $\pm 1.6\,\mathrm{V}$ bias, which is higher than that of In/PPy/Ag junction ($\gamma = 1.2$ at $\pm 3.0\,\mathrm{V}$ bias) because Al has a lower work function than In. According to the thermoionic emission theory, the bigger barrier height is formed, the Schottky diodes can make a more obvious rectifying effect without changes of other conditions. It is noted that the polymers microstructures, dopant type, and doping degree will affect the rectifying effect.[10,14] For example, the Schottky barrier depends on the conductivity of the polymers, a higher conductivity will narrower the depletion layer and result in the tunnelling of electrons through the thinned Schottky barrier, then the $I - V$ characteristic will exhibit a worse rectifying effect.

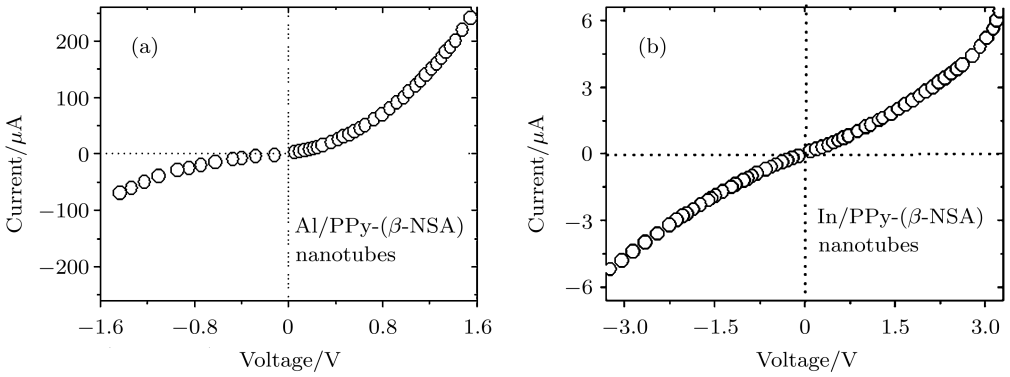


Fig.6. $I - V$ characteristic of diodes at room temperature (a) Al/PPy/Ag (b) In/PPy/Ag.

4. Conclusion

In conclusion, heterojunction diodes made between metals (Al and In) and doped PANI and PPy micro-/nanostructure pellets were fabricated, and obvious rectifying effects have been observed in the $I-V$ characteristic curves. The work functions of metals could be an affective factor of the rectifying effect. As compared to Al/polymer/Ag diodes, the heterojunctions In/polymer/Ag exhibit a lower rectifying ratio. In addition, temperature is also an important factor of rectifying effect, which decreases while the temperature declines possibly due to the increase of polymer resistance.

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