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# ELECTRICAL PROPERTIES OF SCHOTTKY DIODES BASED ON POLY(3, 4-ETHYLENEDIOXYTHIOPHENE) NANOCOMPOSITE BY CYCLIC VOLTAMMETRY

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## Abstract

Three kinds of Schottky diodes based on poly(3,4-ethylenedioxythiophene) nanocomposite were successfully made, respectively, with the metal electrodes such as Al, Zr, and In. Cyclic voltammetry measurement was carried on them. The influence of the work functions of the electrodes, the scan rates etc. on the rectification behavior were thoroughly studied and explained. When the scan rate is too fast above 25mV/s for the nanocomposite with Al electrodes, no electrochemical reaction takes place in the conducting polymer nanocomposite during such a short scan period, and the nanocomposite is not switched on. By comparison with the results of different metals (Al, Zr, In) as the electrode of the

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Schottky barriers at the same voltage and scan rate, the Schottky diode with Zr plate generally has better rectification behavior. Especially, at the Zr electrode, the best rectification performance occurs with the rectification ratio of 1371 at ±2V and the scan rate of 2mV/s, which is pretty high for the conducting polymer/metal Schottky diode. Moreover, when the region of the applied voltage increases, the rectification ratio for Schottky diode at Al electrode increases, but that for Schottky diode at Zr electrode decreases when the voltage range is above ±2V.

## 1. Introduction

Over recent years, there has been significant interest in the fabrication and characterization of Schottky diodes by using organic semiconductors and their derivatives [7, 10]. Bandyopadhyay et al. [1] reported a metal/polymer Schottky diode fabricated from electrochemically prepared free-standing thin films of conducting polyaniline/polycarbonate composite. They also used polyaniline pellets with various metals such as Al, In, Pb, and Sn, and investigated current-voltage characteristics, barrier height, and ideality factor. Campos and Bello [3] have reported I-V and C-V characteristics of metal/poly-*p*-phenylene Schottky diodes over a wide temperature range. Pandey et al. [9] have estimated various electronic parameters such as ideality factor, work function, barrier height, and the Richardson constant through I-V measurement on metal/PANI Schottky junctions.

Schottky diodes based on conjugated polymers have been investigated in the dark and under white light illumination, these systems exhibit a battery in the dark and photo-electrochemical processes under illumination, when tested in a wet atmosphere [2]. The rectification behavior of a polyaniline-based Schottky barrier was used as a sensor for the detection of methane gas [4]. Stable field-effect transistors were fabricated by using water-soluble self-acid doped conducting polyaniline and sulphonic acid ring substituted polyaniline [6].

A Schottky diode can be fabricated in various ways. The conducting polymer can be electrochemically deposited onto the metal electrode, or the metal can be coated onto the free-standing conducting polymer film by vacuum evaporation. Alternatively, the conducting polymer pellet or composite film can be directly pressed onto the metal electrode. The electrodes are usually metals with different work functions for metal/polymer Schottky diodes. Pt and Au with high work function are usually used as electrodes for ohmic contacts. Metals with low work function, such as Al and In are usually used as rectifying contacts.

However, organic semiconductors have low mechanical strengths, which restrict their applications [8]. Composite materials help in overcoming such problems [5, 12]. Composite of conducting polymers with insulating polymers are likely to yield conductive polymeric materials with improved mechanical strengths, while retaining their good electrical conductivities and other properties [8].

Previously, we reported the result of organo-metal diode based on the nanocomposite of the mixture of nanoparticulate poly(3,4-ethylenedioxythiophene) (PEDOT) polymerized in two different systems [11]. In this paper, we study the property of Schottky diodes based on the composite of nanoparticulate PEDOT prepared in DBSA-$FeCl_3$-$H_2O$ system with different metal electrodes (Al, Zr, and In) at different scan rates by using cyclic voltammetry. The Schottky diodes show good rectification behavior and a small 'turn-on potential'.

## 2. Experimental Procedure

### 2.1. Preparation of nano-structured PEDOT

14.692g dodecybenzenesulphonic acid (DBSA) was added into 600ml water and stirred well for an hour. During this period, the micelles of DBSA were formed. Then, 4.266g EDOT was introduced by dropping pipette and stirring continued for half an hour. At the same time, 11.391g $FeCl_3$ as oxidant and dopant was dissolved in 30ml water with cold-water bath to absorb the heat given off by the dissolving procedure. The uniform solution of $FeCl_3$ was poured once into the system. The polymerization was carried out for 48 hours. And then 10 minutes after the reaction stopped, the product automatically separated into an orange, and transparent upper layer and a dark deposit on the bottom. Subsequently, the deposit was collected and washed with water by centrifuge until the washings were colorless, and gave a negative response to aqueous sodium thiocyanate solution. The product was heated in the oven at approx. 60ºC for 24 hours to obtain the dry block.

**2.2. Preparation of PEO-salt matrix**

PEO (polyethyleneoxide) $(\text{M.W.} \approx 5 \times 10^6)$ was slowly added to acetonitrile ($CH_3CN$), and swelled in the solvent for 9 hours to form a uniform gel. $Cu(BF_4)_2 \cdot 6H_2O$ and $LiBF_4$ salts were introduced to the PEO solution, and stirred for half an hour for the ions to spread evenly in the system. The proportions of $Cu(BF_4)_2 \cdot 6H_2O$ to EO and $LiBF_4$ to EO were, respectively, 1:10 and 1:5 in molar ratio. Then, the electrolyte with salts in $CH_3CN$ formed a very bright blue gel matrix.

**2.3. Preparation of PEDOT nanocomposite**

The dry block of PEDOT material was ground into fine powder in a mortar and pestle. The powders were added to the PEO-salt matrix with the proportion of PEDOT as 17.66 wt%. Copper microparticles were introduced into the system with the molar proportion of PEO to Cu equal to 39:1. After the mixing process continued for 2 hours, the solvent was removed by rotary evaporation. The collected product was pressed by the pasta roller for half an hour. The mechanical power further mixed the components of the nanocomposite and made them more uniform. Finally, it was processed into a rubbery, flexible, and black film with a very smooth surface.

**2.4. Schottky diodes preparation**

Three similar squares with the area of $0.5 \times 0.5 cm^2$ were cut from the same PEDOT nanocomposite film, and one side of each square was painted with silver paint. The samples were dried under vacuum for 12 hours. An aluminium plate, a zirconium plate, and an indium plate were, respectively, fixed with a sellotape insulating spacer after cleaning with $CH_3CN$. Then, they were put into the glove box filled with argon together with the copper plates, parafilm, clamps, and the completely dried samples of PEDOT nanocomposite with one surface painted by silver paint. Three Schottky diodes were prepared by the following process in the atmosphere of argon. Each sample of nanocomposite was put into the spacer with the nanocomposite side contacting the metal plate (Al, Zr, In), and the clean copper plate was placed tightly next to the silver layer. The assembly was then wrapped in stretched parafilm and clamped.

## 3. Measurement

The Schottky diodes were measured by cyclic voltammetry at various scan rates and between various ranges of voltage by using an electrochemical measurement unit comprising a Solartron S1 1287 electrochemical interface and Solartron Mobrey 1250 frequency response analyser. During the measurement, the diodes were kept in sealed desiccators with silica gel at room temperature.

## 4. Results and Discussion

### 4.1. Schottky diode based on PEDOT nanocomposite with Al electrodes

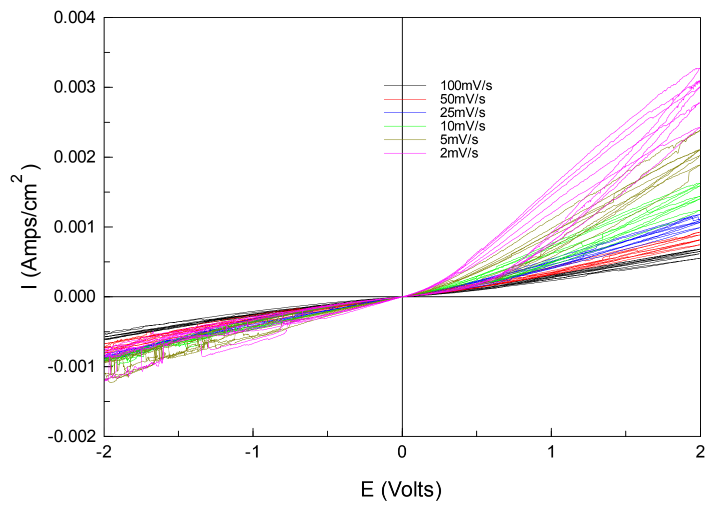


**Figure 1.** Cyclic voltammogram of Schottky diode with Al electrode between –2V and +2V cycled at different scan rates with the PEDOT nanocomposite area of $0.5 \times 0.5 cm^2$ and thickness of 1.204mm.

Figure 1 shows the cyclic voltammetry traces for Schottky diode with Al electrode in the range of ±2V at a series of scan rates measured in the order of 100mV/s, 50mV/s, 25mV/s, 10mV/s, 5mV/s, and 2mV/s (5 cycles at each scan rate). The current was measured from zero to +2V, returning to zero volt (this is called the 'forward cycle'), followed by a similar excursion in the negative bias region (the 'reverse cycle'). Obviously, the plots in

Figure 1 at 100mV/s, 50mV/s, and 25mV/s are perfectly linear in both forward and reverse regions. Over each cycle, the lines overlap with no hysteresis. Presumably, the scan rate is too fast for the nanocomposite at this potential (±2V), so that no electrochemical reaction takes place in the conducting polymer nanocomposite during such a short scan period, and the nanocomposite is not switched on. So, the nanocomposite remains in the insulating state with the resistance of 4000 Ω in both forward and reverse biases.

Moreover, the I-V curves are asymmetrical and non-linear, when the scan rates are 10mV/s, 5mV/s, and 2mV/s. For the 2mV/s, trace a 'turn on' potential in the forward segment of the forward cycle is apparent at approximately 0.75V. Compared with the electrochemical reaction in the forward cycles, the increase in current in the reverse cycles is much smaller. There is only a little noise, when the scan rate is as low as 2mV/s. The device exhibits rectifying behavior due to the formation of the Schottky barrier between the nanocomposite of the conductive state and Al, when the scan rate is below 10mV/s.

**4.2. Schottky diode based on PEDOT nanocomposite with Zr electrode**

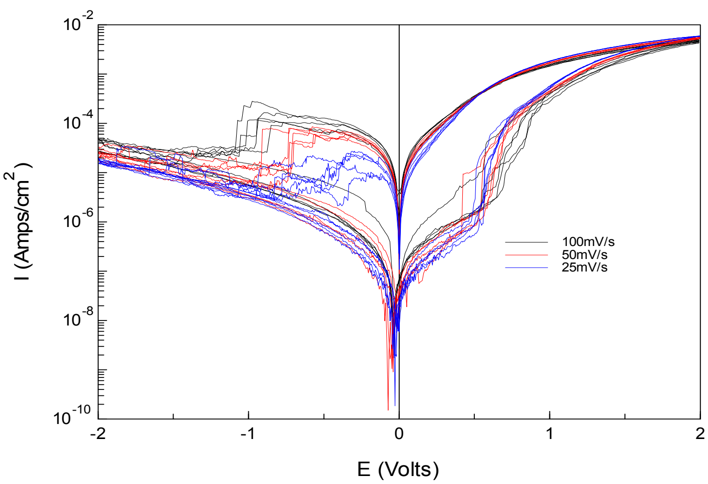


**Figure 2.** LogI vs. E of Schottky diode with Zr electrode between –2V and +2V at the scan rates of 100mV/s, 50mV/s, and 25mV/s with the PEDOT nanocomposite area of $0.5 \times 0.5 cm^2$ and the thickness of 1.204mm.

Figure 2 shows logI vs. E of Schottky diode with Zr electrode between –2V and +2V at the scan rate of 100mV/s, 50mV/s, and 25mV/s with four cycles at each scan rate. There are two 'steps' in this graph, one in the forward region at the voltage of 0.65V, and other in the reverse region at the voltage of approximately –0.97V ~ –0.91V at 100mV/s. The potential between the two voltages is about 1.6V. But, when the applied potentials are above the steps, the trends of current change in the two regions are in the opposite direction. In the forward cycles, the current increases dramatically at the step for the scan rates of 100mV/s, 50mV/s, and 25mV/s. In contrast, in the left part of the graph, the current decreases directly at that crucial point at 100mV/s. The step down in current is apparently in response to the formation of a barrier in the system. The peak in the reverse region also moves to smaller negative potential with decrease in the scan rate and the traces are more 'noisy'. The crucial voltages are, respectively, –0.7V at 50mV/s and –0.3V at 25mV/s.

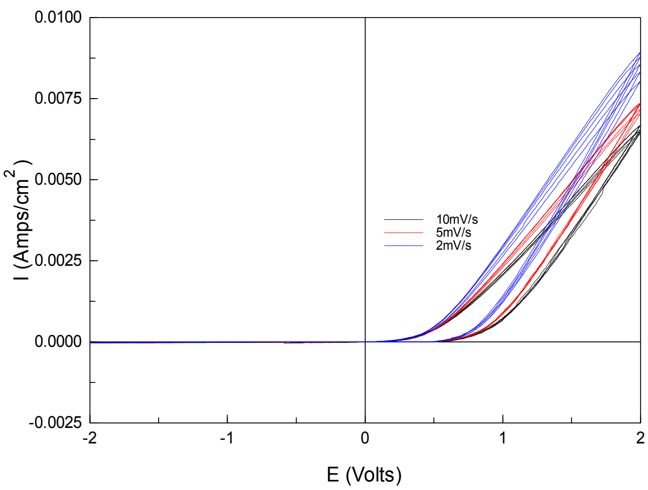


**Figure 3.** Cyclic voltammeter result of Schottky diode at Zr electrode between ±2V at different scan rates with the PEDOT nanocomposite area of 0.5 × 0.5cm$^2$ and the thickness of 1.204mm.

Figure 3 shows the cyclic voltammetry result of Schottky diode based on PEDOT nanocomposite with Zr electrode between –2V and +2V at the scan rates of 10mV/s, 5mV/s, and 2mV/s. It is apparent that, the cycles at 2mV/s are steeper than those at 10mV/s and 5mV/s indicating the nanocomposite becomes more conductive with decreasing scan rate. The 'switch-on potential' is at 0.6V ~ 0.8V in the forward region. The resistance of the nanocomposite above 0.8V is 147 Ω. In the reverse region, the current is as small as $-1.8875 \times 10^{-5}$A, so that the traces can hardly be found since they overlap the E-axis. Furthermore, the 'switch off' peak has initially disappeared.

The system shows excellent rectification behavior with the rectification ratio of 1371, which is the largest observed in this work for PEDOT nanocomposite/metal Schottky diodes with different metal electrodes and different voltage ranges. Hence, excellent rectifying contact has been established with Zr metal plate. This suggests that devices may be easily fabricated by using thin Zr foil.

### 4.3. Schottky diode based on PEDOT nanocomposite with in electrode

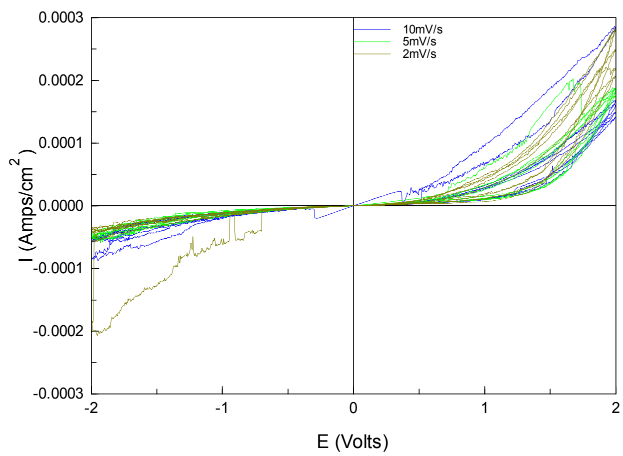


**Figure 4.** CV result of Schottky diode at In electrode between ±2V at different scan rates with the PEDOT nanocomposite area of $0.5 \times 0.5$cm$^2$ and the thickness of 1.204mm.

Figure 4 shows the cyclic voltammogram of Schottky diode based on PEDOT nanocomposite with In electrode between –2V and +2V at the scan rates of 10mV/s, 5mV/s, and 2mV/s successively with five cycles at each rate. In the forward bias, the current changes exponentially and the nanocomposite is switched on in the range of 1V ~ 1.4V. Moreover, except for the second cycle at 10mV/s, there is a clear trend, as before, of steepening slope at lower scan rate. In the reverse bias, the curves almost overlap with the same resistance of $3.53 \times 10^4 \Omega$. Taking the forward resistance at 2V of the last cycle and the resistance of the linear part at –2V, we can calculate the rectification ratio is 21, which is much smaller than Schottky diode with Zr electrode at the same voltage and the same scan rate.

### 4.4. Rectification behaviour

The properties of a contact depend upon the interfacial properties and the difference of work function between metal and semiconductor. A system is called 'a rectifier' of electrical current, if there is a strongly asymmetric flow of electrons through it. Here, rectification behavior is shown by the fabricated Schottky diode of PEDOT nanocomposite with silver as ohmic contact and aluminium, indium or zirconium as Schottky contacts.

It is obvious that, the current increases with the increase of the applied voltage in the forward bias. However, as to the reverse cycle, the change of current keeps linear at all kinds of scan rates with much smaller current than in the forward bias. Asymmetric and non-linear I-V curves of the whole systems show that the devices exhibit rectification behavior. According to the theory of Schottky barrier, the work function of the metal must be smaller than that of the *p*-type semiconductor for the formation of a rectifying barrier at the interface.

The rectification ratio is attributed to the Schottky contact at Al (In, Zr)/nanocomposite. And, the Ag/nanocomposite interface acts as an ohmic contact. In the case of conventional Schottky diode, the current in forward direction is generally of the order of milliamperes (mA), and in the reverse bias, the current is in microamperes (μA) range; that is, there is three orders of magnitude in forward and reverse bias current. Polymer Schottky devices reported so far do not show three orders of magnitude change in forward and reverse bias currents.

**Table 1.** Rectification behavior of Schottky diodes based on PEDOT nanocomposite with various electrodes such as SD-Al, SD-Zr, and SD-In diodes at the scan rate of 2mV/s

| Schottky diodes based on PEDOT nanocomposite with various electrodes | E(V) | Rectification Ratio |
|---|---|---|
| SD-Al diode | 2 | 2 |
| | 4 | 6 |
| | 6 | 11 |
| SD-Zr diode | 2 | 1371 |
| | 4 | 18 |
| | 6 | 11 |
| SD-In diode | 2 | 21 |
| | 4 | 3 |

From the table of the rectification ratio with different electrodes in different voltage ranges at the same scan rate of 2mV/s (Table 1), it is clear that, the voltage and electrodes have influence on the rectification behavior of the Schottky diodes. By comparison with the results of different metals (Al, Zr, In) as the electrode of the Schottky barriers at the same voltage and scan rate, the Schottky diode with Zr plate generally has better rectification behavior. Especially, at the zirconium electrode, the best rectification performance occurs with the rectification ratio of 1371 at ±2V and the scan rate of 2mV/s, which is pretty high for the conducting polymer/metal Schottky diode. Moreover, when the region of the applied voltage increases, the rectification ratio for Schottky diode at Al electrode increases, but that for Schottky diode at Zr electrode decreases when the voltage range is above ±2V.

## 5. Conclusion

Schottky diodes were made by sandwiching PEDOT nanocomposite between the metal plate (Al, Zr, In) and Ag paint and measured by cyclic voltammetry. The I-V characteristics show excellent rectification behavior caused by the nanocomposite/metal Schottky barriers. Especially, the highest rectification ratio was observed to be 1371 with Schottky diode with Zr electrode at ±2V and 2mV/s. In summary, the rectification performance of the polymer/metal Schottky diode depends on the work function of the metal, the switched conductivity of the polymer nanocomposite, the voltage range and the scan rate.

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