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High Field Transport at Interface of Conducting Polymer/Metal Junctions

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Electrical transport properties at interfaces between conducting polymer, poly(3-hexylthiophene), PHT and Al (and Au) in Al/PHT/Au diode have been studied. The interface resistances were directly measured by picking up the potential of PHT near the metal electrodes using micromanipulators equipped in scanning electron microscope. A large potential cliff is observed at Al/PHT interface and an appreciable potential step is also found at PHT/Au interface. The interface resistance at Al/PHT shows the bias and polarity dependencies, indicating the Schottky like junction. At the forward bias, the residual resistance at Al/PHT interface as well as bulk resistance of PHT limits the forward current. At larger reversed biases, the interface resistance at Al/PHT decreased due to the Zener or avalanche breakdown. The detailed bias dependence of the interface resistance at PHT/Au does not indicate simple ohmic contact but the existence of heterogeneous contact to limit the current.

Key words: Interface resistance, Conducting polymers, Metal junctions, Schottky contact, Ohmic contact, High field phenomena

1. INTRODUCTION

Recently, organic materials are intensively studied as electro active elements in opto-electronic devices such as solar cell[1], light emitting diode and transistors[2]. These devices are distinguished from conventional inorganic devices, because of their unique properties such as flexibility, large area and low cost fabrication[3]. However, the fundamental study is still being required to improve the device performances into the commercial level.

It should be realized that functions of the most electronic devices originate from the interfaces such as p-n junction and Schottky junction[3], which are established by making contact with different semiconductors and metals. At the junctions, carrier injection and/or blocking, photo carrier generation and carrier recombination are taking place, resulting in phenomena of rectification, photovoltaic effect and light emission, respectively. The mechanisms of electro-optic functions for conventional semiconductor junctions have been well studied, however, little is known in junctions of organic materials and metals. Therefore, in order to improve the device performance it is important to investigate the detailed electronic structure and transport properties of their interfaces.

In previous paper, we have reported the potential profile in conducting polymer, head to tail poly(3-hexylthiophene), PHT and metals of Al (and Au), namely, Al/PHT/ Au diode and discussed the origin of potential profiles of the diode[4]. In this paper, the interface resistances and the high field transport properties are mentioned for the Al/PHT and PHT/Au junctions. The results suggest that the electrical properties of PHT and metal contact are basically described similarly with the conventional model of inorganic semiconductors, except for the details.

2. EXPERIMENTAL PROCEDURES

Head to Tail coupled poly(3-hexylthiophene), PHT, was purchased from Aldrich Chemical Co. Ltd. The PHT was purified by washing with hexane and methanol for several times. The PHT was dissolved in chloroform by 5wt% and used as cast solution. Figure 1 shows schematic drawing of a planer type diode of Al/PHT/Au. In the fabrication of planer type diode[4], PHT was cast on glass substrate with the thickness of approximately 3 μm, and Au and Al electrodes were evaporated in vacuum with the thickness and width of approximately 30 nm and 2 mm, respectively. The channel length of PHT between Al and Au electrodes was 95 μm.

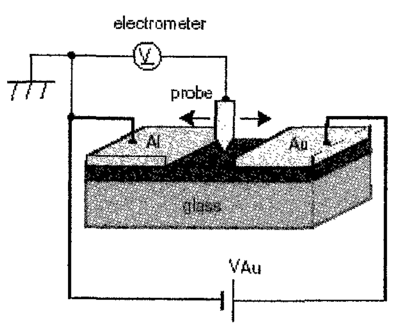

Fig.1 Cell configurations of Al/PHT/Au diode.

The potential probe was prepared with Pt/Ir wire of the diameter of 0.25 mm, which was sharpened by electrochemical etching. The tip radius was approximately 50 nm. The potentials of PHT between Al and Au electrode were measured with the probing tip from Al electrode. In order to pick up the potential at PHT surface, an appropriate pressure of the tip was applied.

3. RESULTS AND DISCUSSION

Current-voltage (*I-V*) characteristics in Al/PHT/Au diode is shown in Fig.2 (a) and (b) for low and high biases, respectively. The polarity of forward bias was positive to Au electrode against Al electrode, which results from the Schottky like junction at Al/PHT and ohmic junction at PHT/Au [5,6]. The ohmic behavior at PHT/Au contact has been confirmed from the linear dependence of *I-V* characteristic in Au/PHT/Au cell [7]. Usually the performance of diodes is indicated by the rectification ratio, namely the ratio of forward current to reversed current at a certain bias. The rectification ratio of the present Al/PHT/Au diode was approximately 200 at ± 5 V. The diode performances in Al/PHT/Au cell have been studied in details[5] and found that the rectification ratio with the magnitude of 10 - 10^6 depending strongly on the contact resistances at both Al/PHT and PHT/Au during the preparation of cell.

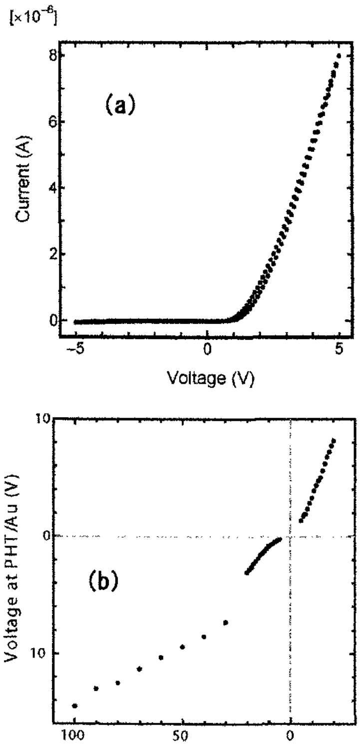

Fig.2 *I-V* characteristics of the Al/PHT/Au diode (a) at low bias and (b) at high bias.

At the higher negative bias down to -100V, the reversed current increases gradually to the magnitude of forward bias as shown in Fig.2 (b). This behavior is somehow similar to that of Zener or avalanche breakdown, in which the current steeply increases at a threshold bias of approximately – 40 V as observed in common inorganic diodes.

Figure 3 shows the potential profiles along the channel for the Al/PHT/Au diode as the parameter of the bias applied to Au electrode. It should be noted that at negative biases a potential bluff appears at the interface of Al/PHT within the distance of 2 μm from the Al edge. The result indicates that most of the bias (more than 95%) is applied to the Al/PHT interface or the depletion layer of the Schottky junction[4]. The thickness of depletion layer is 20-100 nm depending on the impurity or the conductivity of PHT films[8]. At the forward bias, the current increased due to the reduced potential barrier at Al/PHT, resulting in the enhancement of gradient at PHT region and the potential step at PHT/Au.

The conductivity of PHT was estimated to be 2.0×10^{-3} S/cm from the gradient and the dimension of PHT film. The relatively large conductivity is supposed to originate from acceptors of oxygen in the air or trace of oxidative chemical species during polymerization. The PHT is a characteristic of p-type semiconductor, which results in the Schottky like junction by the contact with the low work function metal of Al[5,7].

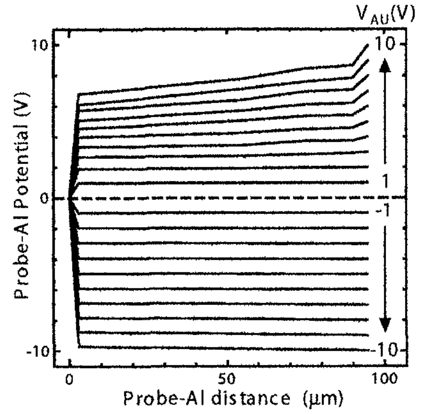

Fig.3 Potential profiles of the Al/PHT/Au diode. The parameters are bias of 1 V step from ± 1V to ± 10 V.

Figures 4 (a) and (b) depict the typical interface resistances at Al/PHT and PHT/Au, respectively, as the function of the voltage appeared across them. As clearly seen for the Al/PHT, the interface resistance depends on the bias and the polarity, indicating the rectification. On the other hand, the interface resistance at PHT/Au was complicated as shown an example in Fig.4(b). This detailed behavior has been obtained clearly by picking up the potential near the Au electrode. The behavior could be hidden in the larger resistances at Al/PHT and PHT bulk region by the measurement between Al and Au electrodes.

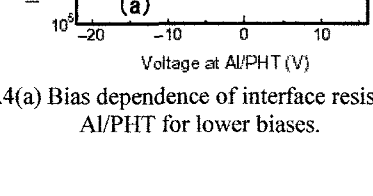

Fig.4(a) Bias dependence of interface resistances Al/PHT for lower biases.

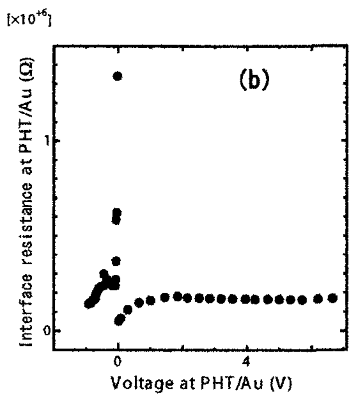

Fig.4(b) Bias dependence of interface resistances at PHT/Au for lower biases.

Curves (a) and (b) in Fig.5 show the bias dependence of interface resistances at Al/PHT and PHT/Au, respectively at higher reversed bias. The sample of Fig.5 was same to that of Fig.4, however, the resistances changed after several days for the preservation. It is clearly shown that the interface resistances at Al/PHT decrease significantly at higher reversed bias and to the almost similar magnitude of forward bias.

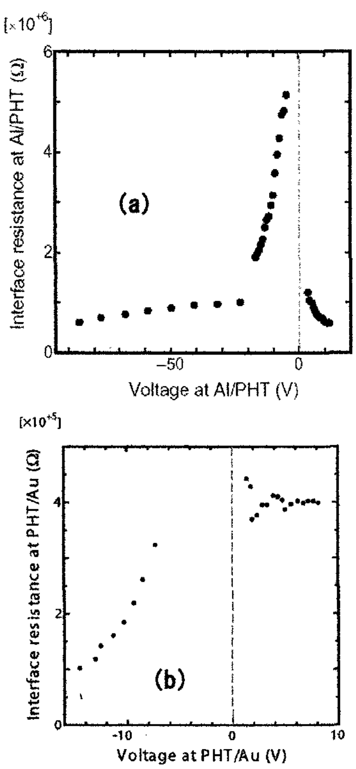

Fig.5 Bias dependence of interface resistances at (a) Al/PHT and (b) PHT/ Au for large bias.

It is interesting to note that the interface resistance at PHT/Au is not constant in detail and depends on the bias and the polarity as shown by another example in Fig.5 (b). The result is somehow different from Fig.4, which is due to variety of surface condition of PHT on the substrate. The fact indicates that the PHT/Au contact is not intrinsically ohmic but composed with the heterogeneous energy levels. The interface resistance at PHT/Au decreases at larger reversed bias, indicating that there are thin insulating potential barriers. The origin of insulating barrier is not clear at present stage, however, may be resulted from decomposition of PHT during the thermal deposition of Au electrodes[7]. It is noted that the interface resistance at PHT/Au is fairly large and determines the diode performance, when a thin film is employed for the case of sandwich type diode[7].

4. Conclusions

Interface resistance and the high field transport properties at the interfaces of poly(3-hexyllthiphene) and metal (Al and Au) junctions have been studied taking the potential profile and their *I-V* characteristic into consideration. It is found that the interface resistances at Al/PHT for the forward bias are appreciable and have to be reduced in order to increase the device performance like solar cell, film transistor et etc. Interface of PHT/Au are not intrinsically ohmic in details.

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