A Study on positive hole injection from electrode to liquid-crystalline semiconductor

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Abstract

Although a liquid crystalline organic semiconductor is characterized by bipolar charge transport with carrier mobility, which is as high as more than $10^{-3}cm^2/Vs$ *and independent of electric field and temperature, it has not been clarified yet how the charge carrier injection from an electrode to a liquid crystalline organic semiconductor is governed. We have studied the current-voltage characteristics of a liquid-crystalline organic semiconductor 2-(4'-Octyphenyl)-6-dodecyloxynaphthalene (8-PNP-O12) in contact with electrodes with different work functions, and have concluded that the observed current is given by thermal positive hole generation at the interface between them in the low electric field region and by the positive hole injection from electrodes to 8-PNP-O12 according the Richardson-Schottky model in the high electric field region. The temperature dependence of the observed current has revealed the formation of an electric double layer at the interface, which depresses the positive hole injection. In order to enhance the positive hole injection, we have modified an Au electrode by a self-assembled monolayer with phenylthiols, and observed dramatic increase in current density. It has been found that the positive hole injection is enhanced with aid of the HOMO levels of phenylthiols, which act as the steps for positive holes to thermally jump from the electrode to the HOMO level of 8-PNP-O12.*

Introduction

Over the past decades, organic semiconductors have emerged as low-cost alternatives to silicon with applications to devices such as photoreceptors for xerographic copiers[1], organic light-emitting devices (OLED)[2-4], organic thin film field-effect transistor (OFET)[5-9], photovoltaic cells[10,11], and radio frequency identification.[12-14] They have thus formed a group of a large number of materials expanding with wide variety from single crystals[2,7-9] with high carrier mobility to amorphous materials, which afford uniform thin films with large area by means of various processes including, not only evaporating,[3,4,10,11,15] but also spin-coating[9,16], dip-casting[17], stamping[18,19], and inkjet-printing[20,21].

The knowledge of the carrier injection from electrodes to organic semiconductors is important for the development of the devices, which need the carrier injection. They include OLED, OTFT, and organic lasers. The physics of carrier injection from electrodes to organic layers, which is thus receiving a great deal of attention, has been reviewed recently[22-24], and is being further extended[25-33]. For charge carrier injection from an electrode to a semiconductor, the Richardson-Schottky[24-36] model and the tunneling one[34,37,38] have been proposed, successfully used to explain many experimental results, and are therefore thought to be available for the analysis of the results obtained in the present study.

Conventional organic semiconductors are polycrystalline or amorphous, and hardly afford layers with both high carrier mobility and large area. It has been found that the carrier transport properties in organic layers are significantly enhanced by use of such liquid-crystalline organic semiconductors as triphenylene derivatives in a discotic columnar phase[39] and 2-phenylbenzothiazole and 2-phenylnaphthalene derivatives in smectic phases,[40,41] both of which are characterized by effective intermolecular π-orbital overlaps and small disorders among hopping sites for carriers owing to self-organization of liquid crystal molecules. In fact, the mobility of carriers in some of these mesophases exceeds 10^{-1} cm^2/V s, being 10-10^2 times larger than those in conventional organic thin films in amorphous state. In addition, liquid-crystalline organic semiconductors are superior to amorphous ones in that the mobilities of carriers depend neither on electric field nor on temperature.[40-43] These characteristics of liquid-crystalline organic semiconductors are quite attractive for the development of new devices requiring faster driving frequencies and lower driving voltages.

Recent studies by use of ultraviolet photoelectron spectroscopy (UPS) on the electronic structure of the interface between a metal electrode and an organic layer by Seki et al. have revealed that an electric double layer is formed at the interface, enhancing the electron injection and depressing the positive hole injection from the former to the latter.[44-52] This result is important for the development of the device with an organic semiconductor, and should be confirmed by the analysis of the current voltage characteristics of the system with the interface. However, it is difficult to do it with an amorphous organic semiconductor under varied electric field and temperature, since the mobility of carriers in it substantially depend on electric field and temperature.

Although the mobility of carriers in liquid-crystalline organic semiconductors is independent of electric field and temperature, the electronic structure and the carrier injection mechanism at their interfaces with electrodes have not yet been studied, since they have been developed recently. It is therefore meaningful to analyze the current-voltage characteristics at the interfaces between electrodes and liquid-crystalline organic semiconductors for the clarification of the electronic structures of the interfaces of electrodes, not only with liquid-crystalline organic semiconductors, but also with usual organic semiconductors.

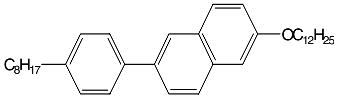
In the previous study, we have analyzed the current-voltage characteristics of a liquid-crystalline organic semiconductor, 2-(4'-Octylphenyl)-6-dodecyloxynaphthalene (8-PNP-O12), in contact with various electrodes, and have revealed that the positive hole injection takes place according to the Richardson-Schottky model.[53,54] The obtained result has proved the proposal by Seki and others that the electric double layer, which depresses the positive hole injection, is formed at the interface between an electrode and 8-PNP-O12 when they are in contact with each other.

In this paper, an attempt has been made to control the electric double layer at the interface of an Au electrode with 8-PNP-O12 by putting a self-assembled monolayer (SAM) with thiophenols on the electrode in order to enhance the positive hole injection according to the reported fact that the positive hole injection from an Au electrode to an amorphous semiconductor was promoted by forming on the electrode a SAM with the electric double layer, which should enhance the positive hole injection.[55,56]

The following two models are considered, depending upon the condition of a SAM on an Au electrode. (A) The positive hole injection is enhanced by the reduction of the work function of the electrode owing to the electric double layer of a SAM. (B) The positive hole injection is enhanced with aid of the highest occupied molecular orbital (HOMO) level of a SAM, which is situated between the Fermi level of the electrode and the HOMO level of 8-PNP-O12 and acts as the step for a positive hole to jump from the former to the latter. It is considered that Model (A) can work when a SAM is thin enough for the tunneling of a positive hole from the electrode to 8-PNP-O12, while Model (B) is still effective when a SAM is too thick for the tunneling. In this study, we have experimentally confirmed the enhancement of the positive hole injection by putting a SAM on an Au electrode in contact with 8-PNP-O12, analyzed its current-voltage characteristics, and estimated the electronic structures of modified Au electrodes and phenylthiols for SAMs by UPS and the condition of a SAM on the electrode by the surface plasmon resonance method.[57]

Experiment

A liquid-crystalline organic semiconductor used in this study was 8-PNP-O12with chemical structure shown in Figure 1. We used Au electrodes without and with modification by SAMs. In order to form SAMs on Au electrodes, we used nitrothiophenol and methylthiophenol, which have in contrast an electron-withdrawing substituent and an electron-donating one, respectively.



Fig,1 Molecular structure of 8 - PNP - O12

The ionization energies (i.e., the energy gaps between the vacuum level and the HOMO levels) of 8- PNP-O12, methylthiophenol, and nitrothiophenol. and the work functions (i.e., the energy gaps between the vacuum level and the Fermi levels) of Au electrodes without and with modification by SAMs were measured at the room temperature by means of UPS with an apparatus AC-1 provided by Rigaku Corporation. With decreasing temperature, 8- PNP-O12 exhibited isotropic liquid state, two mesophases (, i.e., smectic A at 121°C and smectic B at 101°C), and a polycrystalline phase at 68°C. In 8-PNP-O12 in liquid-crystalline state, the electronic conduction is predominant owing to the facts that 8-PNP-O12 with high purity can be easily prepared, and that both electrons and positive holes are highly mobile. Actually, the mobilities of positive holes in 8-PNP-O12 in SmA and SmB phases are $2\times10^{-4}\mathrm{cm}^2/\mathrm{Vs}$ and $1.5\times10^{-3}\mathrm{cm}^2/\mathrm{Vs}$, respectively.

A liquid crystal cell is composed of two parallel Au electrodes evaporated on glass plates. A liquid of 8-PNP-O12 in isotropic phase was filled into the cell with aid of capillary action. The distance between two electrodes in a cell, as adjusted by use of silica spacers, ranged from 4 to 5 μm, and was determined by measuring its capacitance. An Au electrode was modified by a SAM according to the following procedure. Namely, an Au electrode was submerged in a 1×10^{-3} M solution of a thiol in dichloromethane for 20 h at room temperature. Upon removal from the thiol solution, the substrate was rinsed with a 30% methanol in chloroform solution and dried in a stream of dry nitrogen.

Result and Discussion

From the result of the UPS measurement, it has been found that the electronic energy level of the HOMOs of 8-PNPO-12, nitrothiophenol, and methylthiophenol are -5.6eV, -5.3eV, and -5.1eV, respectively, and the Fermi levels of Au electrodes without and with modification by SAMs of nitrothiophenol and methylthiophenol were -4.9eV, -5.1eV, and -4.5eV, respectively. The result of the above-stated measurements is in accord with the fact that a nitro group and a methyl group are electron-withdrawing and electron-donating, respectively, indicating that the result is appropriate. Figure 2 shows the electronic structure of the interface between the electrode and 8-PNP-O12. We assume that the electric double layer is formed at the interface between an Au electrode and a SAM, while it is not formed between a SAM and a 8-PNP-O12 layer.

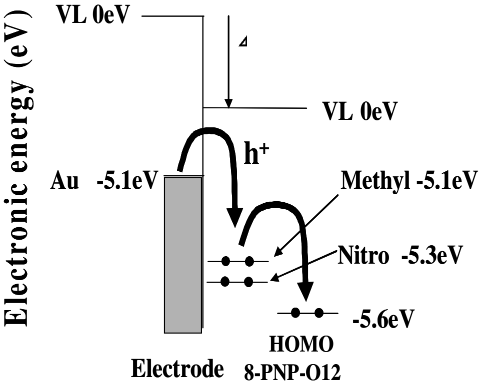
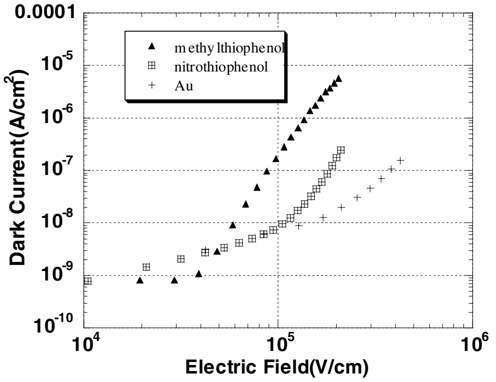


Fig.2 Electronic structure of interface between modified electrode and 8-PNP-O12.

From the above-stated results, it is predicted that the current density due to the injection of positive holes from an electrode to 8- PNP-O12 should be in the order of an Au electrode modified by a SAM of nitrothiophenol, an unmodified one, and the one modified by a SAM of methylthiophenol according to Model (A), and in the order of an Au electrode modified by a SAM of methylthiophenol, the one modified by a SAM of nitrothiophenol, and the unmodified one according to Model (B). In Model (B), it is considered that the enhancement of the hole injection is more extensive when the HOMO level of a thiophenol is closer to the middle point between the Fermi level of an Au electrode and the HOMO level of 8-PNPO-12.

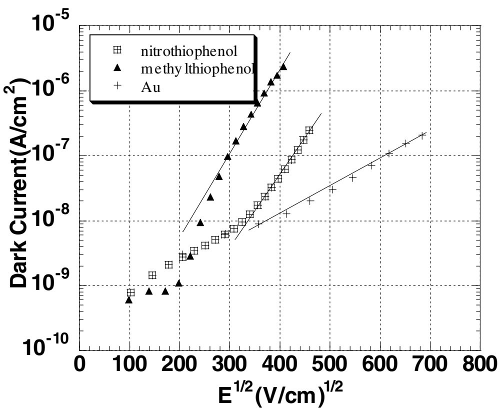
From the result of the surface plasmon resonance measurement, it was found that the surfaces of the modified Au electrodes were completely covered with SAMs with thickness of 4-10 Å .

Figure 3 shows the current-voltage characteristics with Au electrodes without and with modification by SAMs of nitrothiophenol and methylthiophenol. With increasing electric field, we observed an abruptly increasing nonlinear electric current, following an linearly increasing one. As seen in Figure 3, the positive hole injection from an Au electrode to 8-PNPO-12 was enhanced by the SAM-modification.

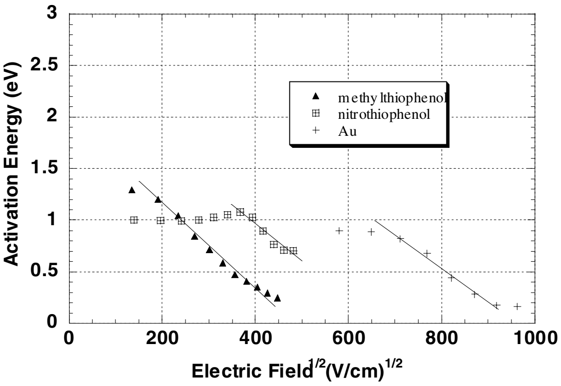


Fig,3 Current-voltage characteristics of the cells with unmodified and modified Au electrodes in contact with 8-PNP-O12.

Figure 4 shows the logarithm of the observed current as a function of the square root of electric field for these electrodes, exhibiting straight lines. The Arrhenius plot of the observed current density in the nonlinear region in each sample exhibits a straight line, slope of which thus gives its activation energy. Figure 5 shows the activation energy as functions of the square route of electric field. As shown in this figure, the activation energy decreased linearly with the square root of electric field in the nonlinear region. The results shown in Figures 4 and 5 indicate that the observed current in the nonlinear region is due to the injection of positive holes from the electrodes to 8- PNP-O12 according to the Richardson-Schottky model.



Fig,4 Schottky plots for the current-voltage characteristics with unmodified and modified Au electrodes in contact with 8-PNP-O12



Fig,5 Activation energy as a functions of square route electric field for the cells with unmodified and modified Au electrodes in contact with 8-PNP-O12.

The threshold of the electric field for the appearance of the nonlinear electric current in Figure 3 was in the order of an unmodified Au electrode, an electrode modified by a SAM of nitrothiophenol, and the one modified by a SAM of methylthiophenol. In addition, the threshold of the electric field for the decrease in the activation energy with the square root of electric field was in the same order. The above-stated result is accord, not with Model (A), but with Model (B). It is considered that Model (B) was dominant in this system, since the SAM was too thick for Model (A) to work effectively.

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