Infrared Absorption Induced by Field Effect from a Metal–Insulator–Semiconductor Diode Fabricated with Regioregular Poly(3-hexylthiophene)

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Infrared absorption induced by field effect from a metal–insulator–semiconductor diode with an Au/aluminum oxide/regioregular poly(3-hexylthiophene) structure has been obtained by using a combination of infrared reflection–absorption spectroscopy and the FT-IR difference-spectrum method. The observed bands have been attributed to carriers (positive polarons) injected into the polymer layer and accumulated near the surface of the layer.

Conjugated polymers have been incorporated as the active semiconductors in field-effect transistors (FETs) with metal–insulator–semiconductor (MIS) structures.[1–3] Among polymer MIS-FETs, the highest hole mobility of 0.1 $cm^2V^{-1}s^{-1}$ has been demonstrated for the FET based on regioregular poly(3-hexylthiophene) (P3HT) to date.[4] In these FETs, carriers are induced by the application of a voltage between the gate and source electrodes, and are strongly associated with the functions of the devices. Since an MIS diode is the most useful device in the study of semiconductor surfaces, studies on MIS diodes will lead us to a better understanding of the properties of MIS-FETs. Carriers in conjugated polymers are charged quasi-particles with structural changes extending over several repeating units. A conjugated polymer having a nondegenerate ground state can support charged quasi-particles such as polarons or bipolarons, which are generated by doping.[5] A polaron has charge $+e$ (or $-e$) and spin 1/2, whereas a bipolaron has charge $+2e$ (or $-2e$) and no spin. Polarons and bipolarons give rise to infrared-active vibrations (IRAVs) and sub-gap electronic transitions. It has been shown that in situ electronic absorption spectrometry is useful in studying carriers and excitons in polymer electronic devices.[4,6,7] Recently, we have demonstrated that infrared reflection–absorption spectroscopy is a powerful tool for the studies of carriers generated in organic light-emitting diodes.[8,9] In this paper, we have measured in situ voltage-induced infrared absorption from the field-effect diode fabricated with P3HT by using a reflection-absorption configuration.

A schematic diagram of an MIS diode based on P3HT is shown in Figure 1a. Gold was thermally evaporated onto a glass substrate and used as the gate electrode. The thickness of the gold layer was about 50 nm. Aluminum oxide was then sputtered onto this gold layer by use of an ANELVA SPF-210B apparatus. Sputtering was performed from an aluminum oxide target under a 20-Pa pressure of argon for 80 min. The RF power was 160 W. A film of regioregular P3HT (Aldrich) was formed on the aluminum oxide layer from a $CHCl_3$ solution of 0.8 wt % by the spin-coating technique. The thickness of the polymer layer was about 120 nm. The top electrode of the device was made in the following two ways. A thin film of gold (thickness, 50 nm) was formed on the polymer layer by heat evaporation for the MIS diodes used for capacitance–voltage measurements. A finger-shaped gold electrode was formed on the polymer layer for the diodes used for infrared measurements. A schematic structure of the finger-shaped electrode is shown in Figure 1b. The width of a finger and the distance between adjacent fingers were about 75 μm. The bias dependence of the capacitance of the MIS diodes was measured on an Agilent Technologies 4263B LCR meter. The voltage-induced infrared spectra from the P3HT MIS diodes were recorded on a Bio-Rad FTS 175 FT-IR spectrophotometer equipped with a linearized MCT detector by using a single attenuated total reflection accessory (Specac Golden Gate). A home-made upper plate was used as the sample stage of the accessory. The incident angle of this accessory was fixed to be 45°. Infrared light was incident on the top electrode of the MIS diode. The reflected light from the device was returned to the spectrophotometer. Voltage-induced infrared spectra were measured by using the FT-IR difference-spectrum method at room temperature. Interferograms from 2000 scans under the application of -10 V ($+3$ V) to the gate electrode with respect to the top electrode were averaged for obtaining the difference spectrum expressed by the following equation:

$$\log\frac{B_3}{B_{-10}} = \log\frac{B_R}{B_{-10}} \times \frac{B_3}{B_R}$$
$$= \log\frac{B_R}{B_{-10}} - \log\frac{B_R}{B_3} = A_{-10} - A_3 = \Delta A$$

where B_{-10} and B_3 are the infrared intensity spectra at -10 and 3 V, respectively; B_R is the reference spectrum.

The capacitance per unit area (C) is plotted against the bias voltage of the gate electrode with respect to the top electrode for the MIS diode with the Au/aluminum oxide/P3HT structure in Figure 2. The C–V curves are useful for obtaining information on the threshold voltage at which carriers are accumulated. The observed C–V curves are similar to that of the MIS diode with the n-Si/SiO_2/P3HT structure reported previously.[10] These curves are characteristic of an MIS diode based on a p-type semiconductor.[11] In the negative bias range, capacitance shows an almost constant value. In this bias region, positive carriers are accumulated near the P3HT/aluminum-oxide interface; the observed capacitance is attributable to the capacitor of the aluminum oxide layer. In the positive bias range, capacitance shows

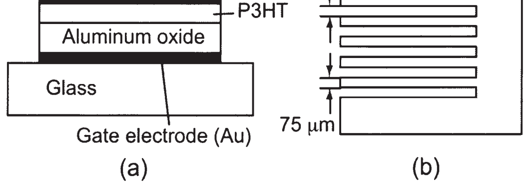

Figure 1. Structures of (a) a metal–insulator–semiconductor diode and (b) a finger-shaped electrode.

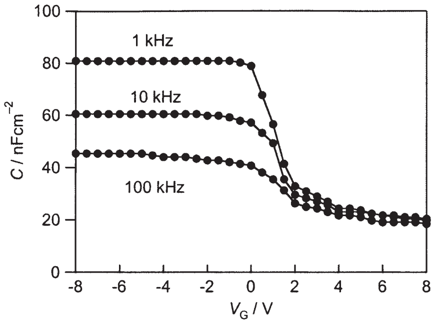

Figure 2. Capacitance vs voltage plots of an Au/aluminum oxide/P3HT diode.

a plateau at a low value; carriers are not accumulated. The observed capacitance originates from the direct series of the aluminum-oxide and the P3HT capacitors. The *C–V* curves show that the threshold voltage is about 2 V. On the basis of these results, we have taken the infrared difference spectrum between −10 and 3 V in order to study the carriers accumulated in the negative bias range.

The infrared spectrum of a P3HT film is shown in Figure 3a. The infrared difference spectrum of the MIS diode based on P3HT between −10 and 3 V is shown in Figure 3b. Positive bands are observed at 1391, 1288, 1273, 1179, 1136, and 1063 cm^{-1}. These bands are attributable to the species generated under the application of −10 V. Although the intensities of the observed voltage-induced infrared bands are extremely weak, the obtained spectrum is reproducible and reliable. In this infrared measurement a half of the incident infrared light has passed through the polymer and the aluminum-oxide layers, whereas the other half has been reflected. Thus, one should make a correction to the observed absorbance change ΔA^{o} for obtaining real absorbance change ΔA^{r} induced by the application of the gate bias. When we take into accounts two kinds of reflected light from the finger-shaped electrodes and the gate electrode, and

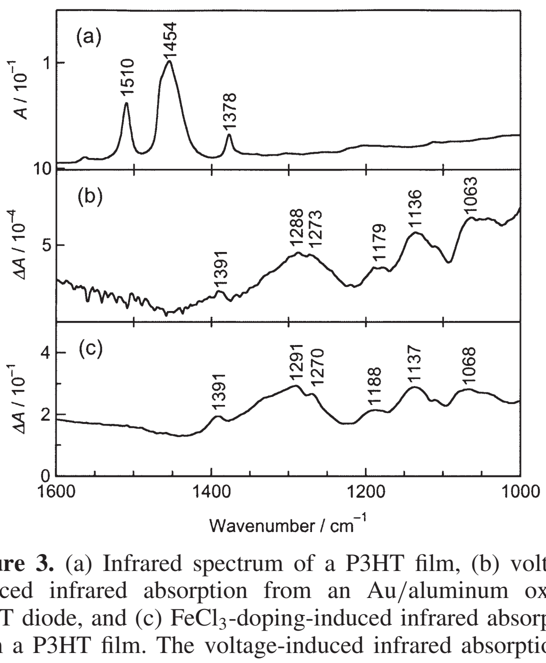

Figure 3. (a) Infrared spectrum of a P3HT film, (b) voltage-induced infrared absorption from an Au/aluminum oxide/P3HT diode, and (c) $FeCl_3$-doping-induced infrared absorption from a P3HT film. The voltage-induced infrared absorption is the difference spectrum between −10 V and 3 V.

the absorbance change is small, ΔA^{r} can be approximately expressed as

$$\Delta A^{r} \approx 2\Delta A^{o}.$$

The ordinate of Figure 3b represents the observed absorbance change. The infrared absorption of a P3HT film doped with a vapor of iron (III) chloride ($FeCl_3$) is shown in Figure 3c. The doping-induced bands are observed at 1391, 1291, 1270, 1188, 1137, and 1068 cm^{-1}. Since iron (III) chloride is an acceptor, positive carriers and $FeCl_4^-$ anions are formed upon $FeCl_3$ doping. Navarrete and Zerbi showed that these doping-induced bands originate from the structural changes from benzenoid to quinoid.[12] The infrared absorption induced by field effect from the MIS diode is quite similar to the $FeCl_3$-doping induced one, although small wavenumber differences are observed. Thus, the observed voltage-induced infrared absorption can be attributed to infrared bands associated with the positive carriers generated in the P3HT layer by field effect. The injected carriers are expected to move to the P3HT/aluminum oxide interface under the electric field. When a thin film of P3HT is doped with $FeCl_3$, two electronic absorption bands have been observed at 1.6 eV and below 0.5 eV. These two bands are attributable to the sub-gap electronic transitions due to positive polarons.[13] The similarity between field-effect-induced and $FeCl_3$-doping-induced infrared spectra means that positive polarons are generated by field effect under the application of −10 V to the gate electrode. The obtained infrared result indicates that positive charge is injected into the P3HT layer and positive polarons are formed and accumulated near the surface of the layer under the application of −10 V. We have demonstrated that in situ infrared reflection–absorption spectroscopy is a powerful tool for the studies of carriers in MIS devices based on a conjugated polymer.

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