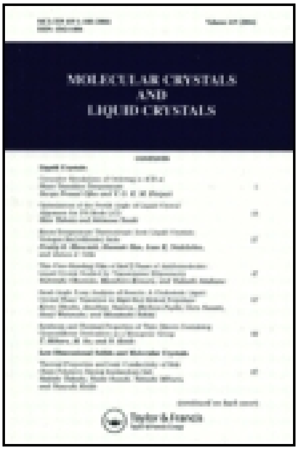

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Influence of the Atmosphere On the Electric Behavior of A Polymeric Field Effect Transistor

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INFLUENCE OF THE ATMOSPHERE ON THE ELECTRIC BEHAVIOR OF A POLYMERIC FIELD EFFECT TRANSISTOR

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A polymer FET device was fabricated with poly(3-hexylthophene) (P3HT) as a active layer and PMMA/PVA bilayer as a gate dielectric. The influence of the measuremental atmosphere on the FET property was investigated. The off-current was increased and the threshold voltage (V_{th}) shifted positively by exposing the device in the air. Investigation of the I_G–V_G behavior and electro-absorption spectra indicated that the observed phenomena were mainly due to the presence of the excess carrier in the active layer which was produced by the oxidation of P3HT. The shift of V_{th} under the air is mainly due to the decrease of the redox potential of P3HT.

Keywords: influence of the atmosphere; leakage current; polymeric FET; shift threshold voltage

INTRODUCTION

An organic field-effect transistor (FET) has been investigated extensively from the standpoint of the flexibility and processability in a large area device. Especially, polymer materials are thought to be promising materials for flexible and low-cost fabrication with wet-process such as spin coating, spray coating, and printing [1–5]. Up to the present, great number of examinations of the polymer FET fabrication is reported although it has still several serious problems. One of the problems is the shift of the threshold voltage (V_{th}) that is known to be significantly depending on the atmosphere of the preparation and the measurement. Exposure of the device

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in the air brings about the increase in the off current indicating the already presence of the carrier in the active layer. It has been reported that the doping of the active layer with oxygen, which adsorbed on the active layer, produces the carrier [6,7]. In contrary to the claim, it was reported that the cause for the influence is the humidity rather than the oxygen in air [8–11]. Therefore, it is important to investigate the origins of the atmospheric effect on the electric behavior of the polymeric FET in detail. In this paper, we have prepared the polymer FET consisting of poly(3-hexylthiophene) (P3HT) as an active layer and PMMA/PVA as a polymer gate dielectric. The influence of the measuremental condition and the effect on the FET property was investigated.

EXPERIMENTS

PMMA and PVA were obtained from Nakalai Tesque, Inc. and were purified with twice reprecipitation. A P3HT was obtained from Aldrich Chemicals Co. Inc and was purified according to literature procedure [12]. The PMMA insulator layer (40 nm) was prepared on an indium doped tin oxide (ITO) glass substrate by dipping method from the chloroform solution, and then dried under the chloroform atmosphere and then dried at 80°C for 8 hours *in vacuo*. An aqueous solution containing 0.1 wt.% PVA was spin-coated on the ITO/PMMA film with 1000 rpm for 60 sec, and then dried at 80°C for 8 hours *in vacuo*. The PVA layer was inserted between the PMMA and P3HT layers to avoid the fusion of P3HT with PMMA at the preparation process. A toluene solution containing 0.2 wt% P3HT was spin-coated on the ITO/PMMA/PVA film with the similar condition as described above. Finally, the source and drain gold electrodes (40 nm) were deposited on the ITO/PMMA/PVA/P3HT film. The electrodes were patterned with a 5 mm of length and a 0.1 mm of width and leave a 20 μm space through a metal mask. Then the channel length of the FET was 20 μm, and the channel width was 5 mm. The current-voltage characteristics of all cells were measured with a Keithley 4200 Parameter Analyzer under the vacuum at 10^{-3} Pa, the N_2 flow and the air atmosphere. All experiments were carried out at room temperature.

RESULTS AND DISCUSSION

Figure 1(A) shows the I_{DS}–V_{DS} properties of the prepared polymer FET under the vacuum, the N_2 flow, and the air atmosphere. In any cases, the modulation of the drain current (I_{DS}) was clearly observed. However, the clear saturation behavior of the I_{DS} was not observed at the N_2 and the air atmosphere, and the higher I_{DS} was obtained as compared with that

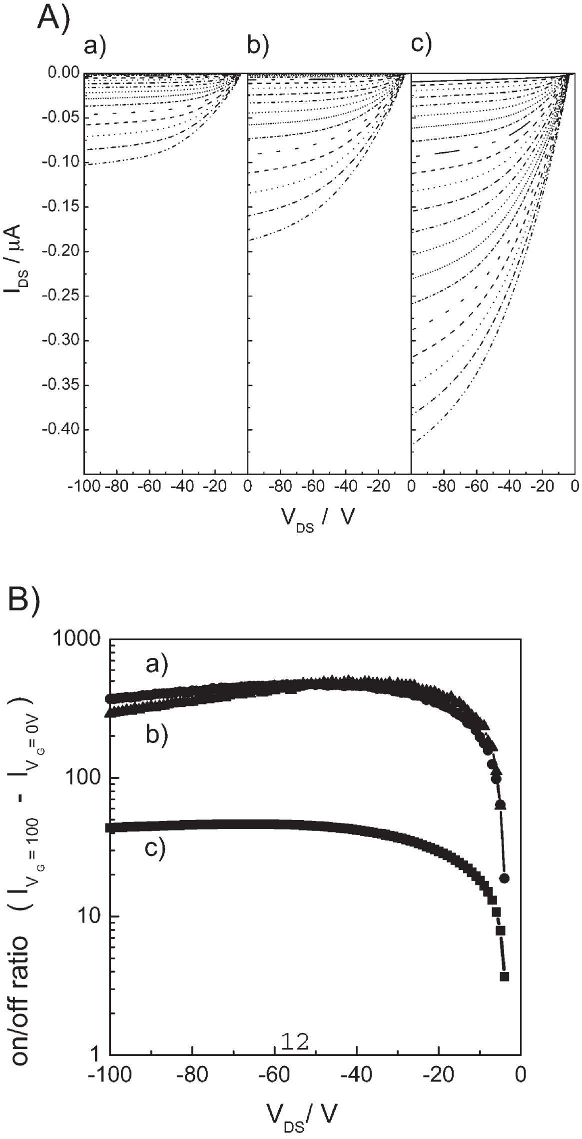

FIGURE 1 The I_{DS}-V_{DS} properties A) and the on/off ratio vs. V_{DS} plots B) of the polymer FET under a) the vacuum, b) the flow N_2, and c) the air atmosphere.

under the vacuum. Particularly, I_{DS} at zero gate voltage (V_G), i.e., the off-current, was considerably increased under the air. Therefore, the on/off ratio (on: I_{DS} at $V_G = 100\,V$, off: I_{DS} at $V_G = 0\,V$) under the air was lowest in this study (Fig. 1(B)). It suggests that the large off current is mainly due to the humidity or the oxygen in the air.

It is known that the threshold voltage (V_{th}) under the vacuum shifts in the direction to the positive voltage by exposing a device in the air [8–10]. We have also observed the positive shift of the V_{th}under the air (Fig. 2). Probably, the difference between the V_{th} under the vacuum and N_2 is due to the interfusion of the tiny amount of the air. However, it is not cleared why the high off current and the shift of $V_{th}$was observed.

In order to investigate the influence of the air on the properties, the current between the source and gate electrodes (I_G) was monitored. The I_G–V_G properties of the device under the vacuum and the air atmosphere were shown in Figure 3. As a reference, the device without an active layer was also prepared. Its I_G–V_G property was also shown in Figure 3. In any cases, the hysteresis of I_G could be observed. It was stable at least 10 cycles. However, the amount of the charge flow in the device, i.e., the area of the hysteresis curve, was larger than that of the device without an active layer. It indicates that the hole is injected from the source electrode to the P3HT layer. Namely, the hysteresis is caused by the accumulation and release of the hole in the device. Under the air, the larger amount of the injected charge was observed as compared with that under the vacuum, suggesting the increase of the accumulation.

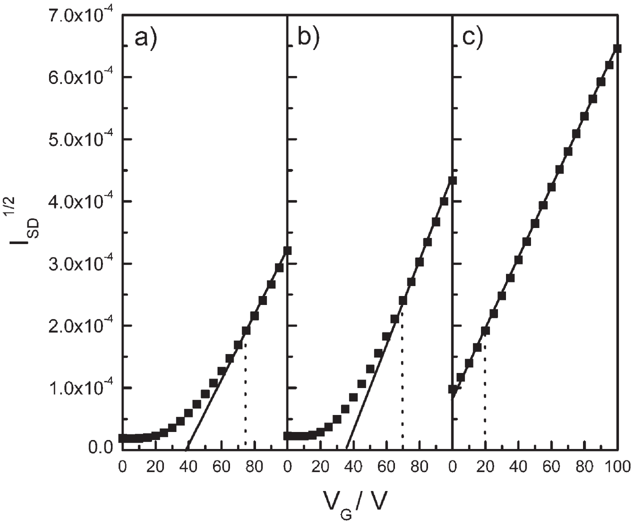

FIGURE 2 The $I_{DS}^{1/2}$-V_{DS} properties of the polymer FET under a) the vacuum, b) flow N_2, and c) the air atmosphere.

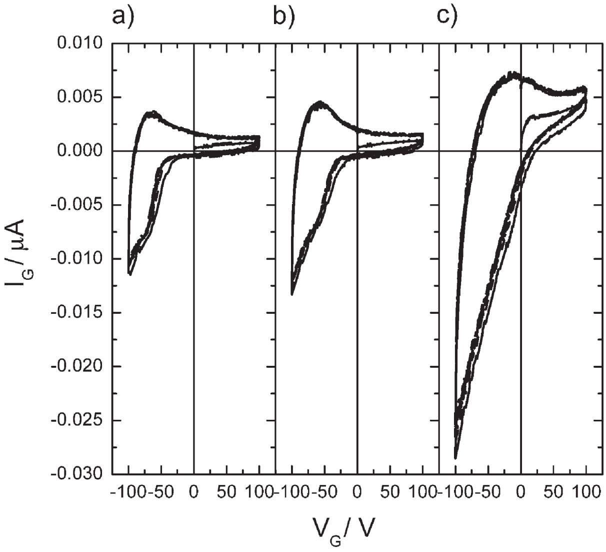

FIGURE 3 The I_G–V_G properties of the polymer FET under a) the vacuum, b) flow N_2, and c) the air atmosphere. (10 cycle)

The hysteresis curve measured in the vacuum showed a cathodic shoulder and an anodic peak at ca. −75 V. Similar shoulder and peak was also observed under the N_2 and the air at ca. −70 and ca. −20 V, respectively. Since the shoulder and the peak in the voltage sweep means the presence of the diffusion-controlled charge transfer [13–15], it can be considered that the voltage is the oxidation and reduction (redox) potential of the P3HT in this study. On the other word, the P3HT was oxidized at the applied voltage, and the oxidized P3HT was accumulated in the device. These oxidative voltages well corresponded to the each initial voltage in the linear region of the $I_{DS}{}^{1/2}$ vs. V_G plots, as shown in Figure 2. The initial voltage means the formation of the channel for the carrier transport between the source and the drain electrodes [16]. Namely, the channel was formed resulted in the oxidation of the P3HT. Under the air, the oxidation of P3HT is taken place at lower voltage as compared with that under the vacuum and N_2. It indicates the channel is formed before the applying the V_G. Such case, the high off-current and the positive shift of V_{th} are observed by the formation of the channel at below $V_G = 0$ V.

It becomes important to confirm whether the P3HT is oxidized at the voltage. Figure 4 shows absorption spectrum and the change of the absorbance at 500 and 800 nm of the sandwich type device consisting of ITO/PMMA (400 nm)/PVA (5 nm)/P3HT (400 nm)/Au (200 nm) upon the applied voltage under the air. The absorbance was not changed from

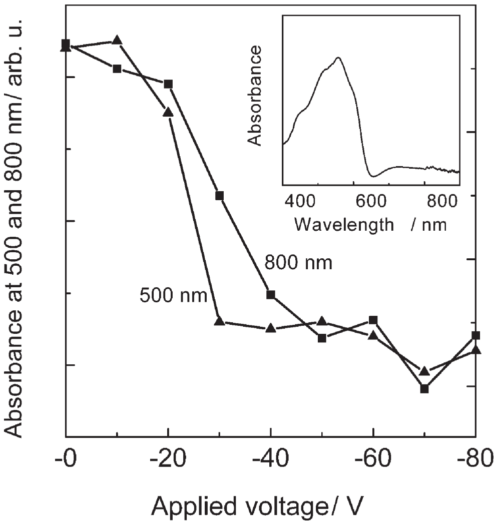

FIGURE 4 The change of the absorbance of ITO/PMMA (400 nm)/PVA (5 nm)/P3HT (400 nm)/Au (200 nm) upon the applied voltage. Inset shows the absorption spectrum.

0 to – 20 V. However, it was intensively decreased at ca. – 20 V. and then remains constant at more than – 30 V. It is known that the absorption spectrum of P3HT film is changed by the oxidation and reduction [17]. It can be considered that the decrease of the absorbance at –20 V is due to the oxidation of the P3HT. The voltage of the absorption change in Figure 4 well correspond to the voltage at which the shoulder and peak of the I_G appeared (Fig. 3) and the initial voltage of $I_{DS}{}^{1/2}$ vs. V_G plot in Figure 2. All were $V_G = -20$ V under the air. The result is consistent with our proposed mechanism for the increase of the off-current and the shift of the V_{th}. It is indicated that the increase of the off current and the shift of V_{th} under the air is due to the decrease of the redox potential of P3HT. As is often reported that the oxygen adsorbed on the active layer caused oxidization of the P3HT, then the effect of the oxygen should be one of the important reason why the decrease of the redox potential of the P3HT. However, the effect of the water also should be an origin of it because it often helps ion conduction that helps the redox reaction.

CONCLUSION

A polymer FET device was fabricated with poly(3-hexylthiophene) as an active layer and PMMA/PVA bilayer as a gate dielectric. In order to investigate the influence of the measurement condition, properties of the device was evaluated under the vacuum, N_2 and the air atmosphere. Under the air, the high off-current and the positive shift of V_{th} were observed as compared with that under the vacuum and N_2. The hysteresis in the plots of the I_G vs.V_G showed the shoulder and peak contributed to the redox of the P3HT. Under the air, the voltage observed the redox agree with the initial voltage in the linear region of the $I_{DS}^{1/2}$ vs. V_G plots, indicating the channel formed with the oxidized P3HT. The generation of oxidized P3HT was confirmed with the electro-spectroscopic measurement. From these results, it is cleared that the increase of the off-current and the shift of V_{th} under the air is due to the decrease of the redox potential of P3HT.

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