Influence of Contact Barrier Height on the Characteristics of Polymer Field-Effect Transistors

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We investigated the influence of contact barrier height on the performance of polymer field-effect transistors (FETs) by using metals with work functions closely matching the electron and hole transport levels of the polymer or by adjusting the individual HOMO/LUMO levels of the polymer layer. No clear relationship between the bulk mobilities measured by time-of-flight method and the field-effect mobilities calculated from saturation drain current was found in the present study. In contrast, the field-effect mobilities in π -conjugated polymers used in this study show a tendency to slightly increase with a decrease in carrier injection barrier.

Keyword: organic field-effect transistor, mobility, carrier injection, π -conjugated polymers

1. Introduction

Main-chain π -conjugated polymers belong to one of the most promising organic materials useful for the fabrications of organic field-effect transistors (OFETs). Extensive studies on poly(*p*-phenylenevinylene) derivatives and poly(dialkyl-fluorene) copolymers have been performed and those classes of polymers have been recognized as processable and robust materials useful for electronics applications [1,2].

In order to achieve high performances in polymer FETs, high carrier mobility and efficient carrier injection from the source electrodes are necessarily required. The former has been already achieved by using polymers with a high degree of regularity [3]. It is considered that the latter can be achieved either by using metals with work functions closely matching the electron and hole transport levels of the polymer or by adjusting the individual highest occupied molecular orbital (HOMO) or lowest unoccupied molecular orbital (LUMO) levels of the polymer layer [4–9]. Therefore, investigating the effect of carrier injection barrier on a performance of polymer FETs is of great importance. In this study, we fabricated FETs using π -conjugated polymers as

the active material and investigated the influence of contact barrier height on the characteristic of polymer FETs.

2. Experimental

2.1. Materials

The π -conjugated polymers used in this study are shown in Fig. 1. The synthesis and purification of poly(2-(9',9'-dihexylfluorenyl)-1,4-phenylene vinylene) (DHF-PPV), poly(2-(7'-methoxy-9',9'-dihexylfluorenyl)-1,4-phenylenevinylene) (MDHF-PPV) and poly(2-(7'-cyano-9',9'-dihexylfluorenyl)-1,4-phenylenevinylene) (CNDHF-PPV) were as described previously [10]. Poly(9,9'-dioctyl-fluorene-co-bithiophen), (F8T2), was used as received from American Dye Source, Inc. Poly(2-methoxy-5-(2'-ethylhexoxy)-1,4-phenylenevinylene), (MEH-PPV), was purchased from Aldrich and also used as received. The highest occupied molecular orbital (HOMO) energy levels were determined by photoemission spectroscopy (AC-2, Rikenkeiki) using spin-cast films on an indium-tin-oxide electrode.

2.2. Fabrication of organic field-effect transistors

We fabricated the two kinds of OFET shown in

Fig.1. Molecular structures of π -conjugated polymers used in this study and HOMO energy levels in the polymers.

Fig. 2. For the bottom gate configuration, a clean glass was used as a substrate and gold was sputtered through a shadow mask to form a 5 mm-wide and 30 nm-thick line as a gate electrode. The poly-chloro-*p*-xylylene (diX-C, Daisankasei Co. Ltd.) was deposited by CVD with a thickness ranging from 470 to 620 nm to serve as a gate insulator for OFETs [11]. The polymeric semiconductors, MEH-PPV, and DHF-PPVs were spin-coated with thickness ranging from 40–60 nm from a chloroform solution onto the dielectric layer. The Au source-drain electrodes with an interdigitated configuration were deposited through a shadow mask. The channel length L and width W were 100 μm and 5 mm, respectively.

For the top gate configuration, a clean glass substrate was spin coated with a polyamic acid precursor solution (Nissan SUNEVER150) and then baked at 280 $^{\circ}\text{C}$ for 1h to achieve full imidization. The source-drain electrodes composed of Au or Pt were formed on the substrate using conventional photolithography and lift-off techniques. The channel length L and width W were 75 μm and 5 mm, respectively. Film with a thickness ranging from 40 to 50 nm of F8T2 was prepared by spin-coating from chloroform solution. The film was annealed under N_2 atmosphere at 280 $^{\circ}\text{C}$ over a period of $\frac{1}{2}$ h followed by quenching to room temperature. Polydomain glassy-nematic emerged with thermal annealing. A gate insulator, diX-C, was deposited by CVD. Finally a gold gate electrode was sputtered through a shadow mask. All devices were temporarily exposed to air prior to the measurement, and characterized using Agilent 4156C Precision Semiconductor Parameter Analyzer in a vacuum atmosphere again.

Fig.2. Schematic cross section of OFETs, (a) bottom gate configuration (b) top gate configuration.

2.3. Time-of-flight measurements

For the time-of-flight (TOF) measurements, a semitransparent aluminum electrode (20 nm thickness) was vacuum deposited on the glass substrate through a shadow mask (2 mm width). On top of the substrate, three DHF-PPVs and MEH-PPV films were prepared by drop casting from their respective toluene solutions. The thicknesses of the four polymer films were 2.5–3.6 μm as measured with a Dektak 3 surface profiler. Residual solvent was removed by heating the samples in vacuum for 3 h at 60 $^{\circ}\text{C}$. An aluminum top electrode (40 nm thickness) was deposited onto the polymer layer through a shadow mask defining the sample area as 2×2 mm. Details of TOF measurements can be found in our previous report [12].

3. Results and Discussion

3.1. Organic field-effect transistors based on DHF-PPVs

Plots of drain current I_D versus drain voltage V_D are shown in Fig. 3(a) as function of applied gate voltage V_G when DHF-PPV is used as an active channel layer. A p-channel FET operates in the accumulation mode on application of a negative bias to a gate electrode, as the concentration of holes contributing to I_D increases. For the V_D greater than the V_G , drain current tends to saturate due to the pinch off the accumulation layer, and is modeled by the equation,

$$I_D = \frac{WC_i}{2L} \mu (V_G - V_T)^2$$

where C_i is the capacitance per unit area of the insulating layer, V_T is the threshold voltage and μ is the field-effect mobility [13]. Above the V_T ,

Fig. 3. (a) Plots of the I_D versus V_D at various V_G values for the OFET using DHF-PPV as a semiconductor. (b) Plots of the I_D (left) and square root of I_D (right) versus V_G at V_D of -100V.

μ can be calculated from the slope of the plot of $|I_D|^{1/2}$ versus V_G . From the plot in Fig. 3(b), a field-effect hole mobility was calculated to be $2.3 \times 10^{-4} \text{ cm}^2/\text{Vs}$, while V_T was -50 V. A field-effect hole mobility was calculated to be $6.5 \times 10^{-4} \text{ cm}^2/\text{Vs}$ for MDHF-PPV. As reference, a FET using MEH-PPV was also fabricated and field-effect hole mobility of $6.0 \times 10^{-4} \text{ cm}^2/\text{Vs}$ was obtained. No field-effect was observed in the FET

Fig. 4. Electric field dependence of the hole mobilities measured in DHF-PPV, MDHF-PPV, MEH-PPV and CNDHF-PPV at 298 K. The lines are fits to Poole-Frenkel model.

with CNDHF-PPV as an active layer, even when either negative or positive gate bias is applied. Both hole and electron mobilities in CNDHF-PPV are assumed to be much lower than those in DHF-PPV and MDHF-PPV. The presence of a strong electron-withdrawing CN group in CNDHF-PPV may act as deep traps for hole carriers. The parameters obtained for these materials are summarized in Table 1.

Interestingly, a clear relationship between bulk mobilities shown in Fig.4 and field-effect mobilities was not found in the present study. In contrast, the field-effect mobilities in four PPVs show a tendency to slightly increase with a decrease in carrier injection barrier. MEH-PPV with lowest hole injection barrier from Au electrodes has relatively high field-effect mobility in spite of its low bulk mobility. These results suggest that the field-effect mobility has little relation to carrier mobility for bulk organic semiconductors. On the other hand, the efficient carrier injection tends to increase the field-effect mobilities in our experimental results.

Table 1. Electrical parameters obtained from FET measurements.

polymer	Field-effect hole mobility (cm ² /Vs)	Threshold Voltage (V)	On/off	HOMO-Au workfunction (eV)	Bulk hole mobility (cm ² /Vs) ^a
DHF-PPV	2.3×10^{-4}	-50	10^2	0.6	1.1×10^{-4}
MDHF-PPV	6.5×10^{-4}	-32	10^3	0.5	4.9×10^{-5}
CNDHF-PPV	No field-effect			0.8	3.9×10^{-8}
MEH-PPV	6.0×10^{-4}	-6.6	10^3	0.1	5.7×10^{-7}

^a Calculated from Fig.4 at electric field 100 (V/cm)^{1/2}.

Fig. 5. Output characteristics for p-channel OFET based on polydomain glassy-nematic F8T2 using (a) Pt source-drain electrodes, (b) Au source-drain electrodes.

3.2. Organic field-effect transistors based on polydomain glassy-nematic F8T2

Figure 5(a) shows the output characteristics of F8T2 FETs using Pt source-drain electrodes. From the saturation current, the field-effect hole mobility was calculated to be $0.021 \text{ cm}^2/\text{Vs}$ while V_T was -12 V . This value is one of the highest values in OFETs using F8T2 as organic semiconductor. On the other hand, Fig. 5(b) shows the output characteristics of F8T2 FETs using Au source-drain electrodes. From the saturation current, the field-effect hole mobility was calculated to be $0.010 \text{ cm}^2/\text{Vs}$ while V_T was -26 V . The work functions of Pt and Au were found to be 5.65 and 5.10 eV, respectively, indicating little hole injection barrier from Pt to HOMO of F8T2 (5.5 eV). A simulation result obtained by other group has shown that a high injection barrier between the source electrodes and the organic semiconductor results in a large decrease in field-effect mobility [14]. The two times of magnitude increase in field-effect hole mobility over the case of the Au

source-drain electrodes is apparently due to the small barrier for hole injection from Pt to HOMO of F8T2.

4. Conclusion

Contact barrier height can have an important effect on the output characteristics of OFETs. A clear relationship between the bulk mobilities measured by time-of-flight method and the field-effect mobilities calculated from saturation drain current was not found in the present study. In contrast, the field-effect mobilities in π -conjugated polymers used in this study show a tendency to slightly increase with a decrease in carrier injection barrier.

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