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Mobility Improvement in N-Type Organic FET with Hetero-Layered Structure

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The field-effect mobility in n-type fullerene field-effect transistors was improved by the hetero-layered structure including the interfacial layer of organic semiconductor between the insulator and channel semiconductor. Various types of hole transporting material were employed for the interfacial layer. The device showed high electron mobility exceeding 1 cm^2/Vs *that was better than that for the substrates with conventional surface treatments, for example, hexamethyldisilazane (HMDS) and octadecyltrichlorosilane (OTS). These results suggest that the electron-donating character of the hole transporting materials leads to filling the electron traps at the insulator interface.*

Keywords: fullerene; hetero-layered structure; high electron mobility; hole transport material; organic field-effect transistor

INTRODUCTION

In recent years, organic transistors have attracted much attention due to their advantages in developing low-cost, flexible, and large-area production. So far, many kinds of organic materials have been reported to achieve high-performance organic field-effect transistors (OFETs) [1–3]. There are two types of organic semiconductors, p-type and n-type, whose majority carriers are holes and electrons, respectively. However, the performance of n-type OFETs are generally inferior to that of p-type. Recently, various n-type organic materials have been developed and high electron mobility with high on–off ratios have been realized [4–7].

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The field-effect mobility of the organic semiconductor is also affected by the device fabrication process. Various methods on surface treatments have been reported to improve the carrier mobility [8–11]. In particular, n-type material in OFETs is very sensitive to the surface modification. Chua *et al.* pointed out that this tendency is due to the surface electron traps of the gate insulator, and if electron traps can be perfectly eliminated, almost organic semiconductors can be operate in n-type mode [12]. Therefore, it has been believed that the gate insulator surface should be as possible as inert to achieve high mobility in n-type OFETs.

In this paper, we propose a hetero-layered structure OFET including an interfacial layer of electronic active organic semiconductor between the insulator and channel layer to improve the field-effect mobility in n-type OFETs. For the channel layer, we employed C_{60}, which is the most standard n-type organic semiconductor, and is reported to show the highest electron mobility for the device fabricated in ultra high vacuum condition [13–17]. For the interfacial layer, we employed two types of hole transporting materials, *m*-MTDATA and NPD, which are generally used for organic light-emitting diodes [18].

Such a hetero-layered OFETs composed of p-type and n-type organic semiconductors have been known as ambipolar organic transistors, which are aimed at the simple inverter circuit or organic light-emitting transistors [19,20]. On the other hand, our proposed hetero-layered OFET is composed of n-type organic semiconductor and hole transporting material showing no FET modulation by itself. The interface layer is expected to eliminate the surface electron traps by the electron-donating character.

EXPERIMENT

The C_{60} was purchased from Tokyo Chemical Industry Corp, N,N′-Bis(1-naphthyl)-N,N′-bis (phenyl)-benzidine (NPD) was purchased from Sigma Aldrich Japan, and 4,4′,4″-tris(3-methylphenylphenylamino) triphenylamine (m-MTDATA) from Luminescence Technology Corp. Figure 1 shows the hetero-ayered structure OFET with top contact and the molecular structures of *m*-MTDATA and NPD. Organic transistors were fabricated on a heavily doped Si substrate with SiO_2 layer (300 nm) that works as a common gate electrode. The substrates were thoroughly washed with water, acetone, isopropanol and UV–O_3 treatment. The interfacial semiconductor layer of *m*-MTDATA and NPD (20 nm ~ 30 nm) were deposited by thermal evaporation under a pressure of 10^{-5} Pa. For the comparison, the substrates with well-known

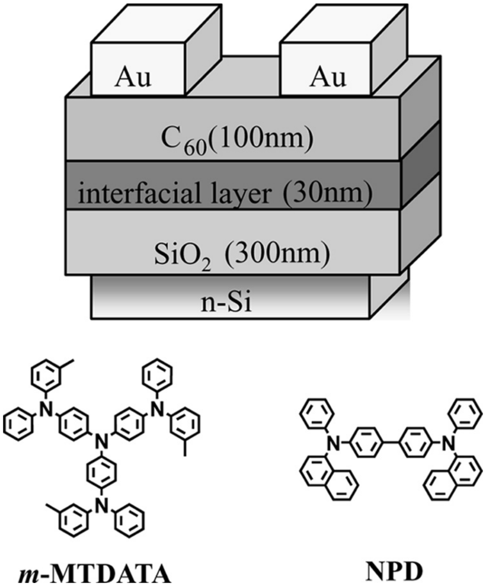
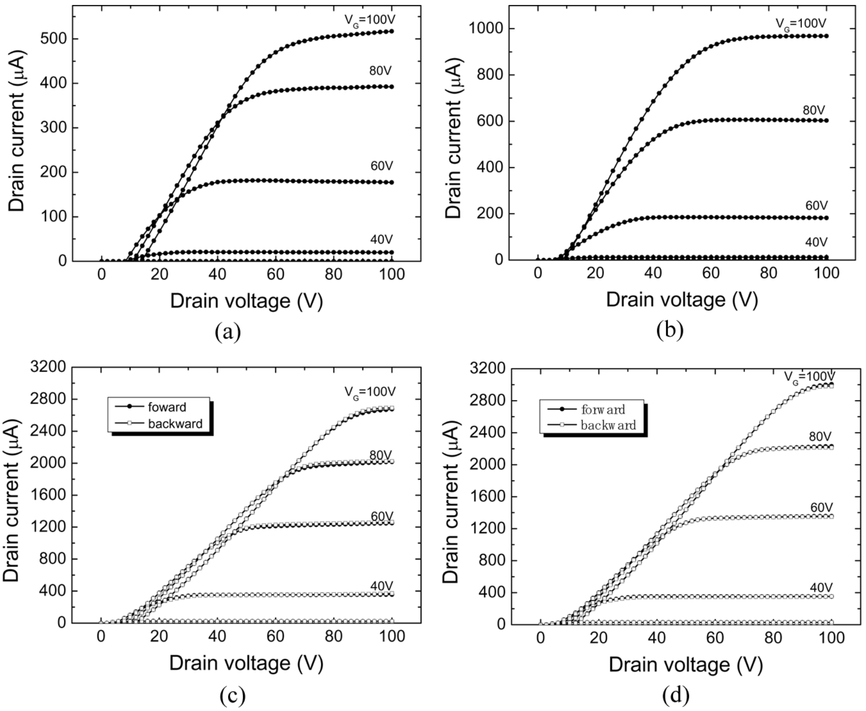


FIGURE 1 The device configuration of OFETs with hetero-layered structure and molecular structures of *m*-MTDATA and NPD.

surface treatment by octadecyltrichlorosilane (OTS) and hexamethyldisilazane (HMDS) were also prepared [9–11]. They were immersed into the OTS or HMDS solution in toluene (1 vol%) for 12 hours. The n-type organic semiconductor of C_{60} was deposited on these substrates with a thickness of 100 nm. Deposition rate was $0.03 \sim 0.05$ nm/s for C_{60} and $0.2 \sim 0.3$ nm/s to *m*-MTDATA and NPD, respectively. Au source and drain electrodes were deposited through a shadow mask. Channel length and width were defined to 50 μm and 5.5 mm, respectively. The current modulation of OFETs were measured by a semiconductor parameter analyzer (Agilent 4155C) in the glove box, where the concentration of oxygen and water were less than 1 ppm.

RESULTS AND DISCUSSION

Figure 2 shows the drain current–drain voltage (I_D–V_D) characteristics of the hetero-layered OFETs with *m*-MTDATA and NPD interfacial layer, and the single layer normal C_{60} OFETs on OTS-treated, HMDS-treated, and non-treated substrates. All the devices showed source-drain current modulation for positive bias of gate voltage, indicating n-type modulation of OFETs. Thus, the hetero-layered OFETs

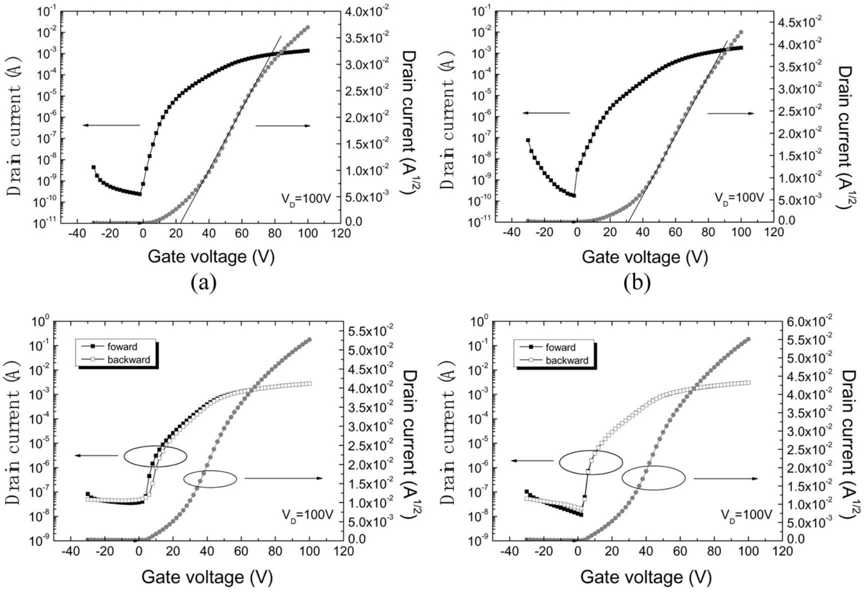


(a) (b) (c) (d)

FIGURE 2 Output characteristics of OFET devices of C_{60} film on the various kinds of surface, (a) OTS, (b) HMDS, (c) *m*-MTDATA (20 nm) films, and (d) NPD (30 nm).

succeeded in n-type modulation and clear saturation with a large drain current over 2 mA. The transfer (I_D–V_G) characteristics of the devices measured at saturation regime ($V_D = 100\,V$) are shown in Figure 3. The I_D–V_G curves for the hetero-layered devices increased only for positively biased gate voltage. This means that they did not operate as an ambipolar transistor, and the interfacial layer of the hetero-layered device did not work as a channel layer. We also show modulation curves of both forward (increasing gate voltage) and backward (decreasing gate voltage) sweeps in the OFETs with *m*-MTDATA and NPD interfacial layer. They are almost identical and very small hysteresis is observed.

The field-effect mobility, threshold voltage and on/off ratio were estimated from the equation of saturation regime, $I_D = [(WC\mu)/2L](V_G - V_T)^2$, where C is the capacitance per unit area of the gate dielectrics, W is the channel width, L is the channel length,



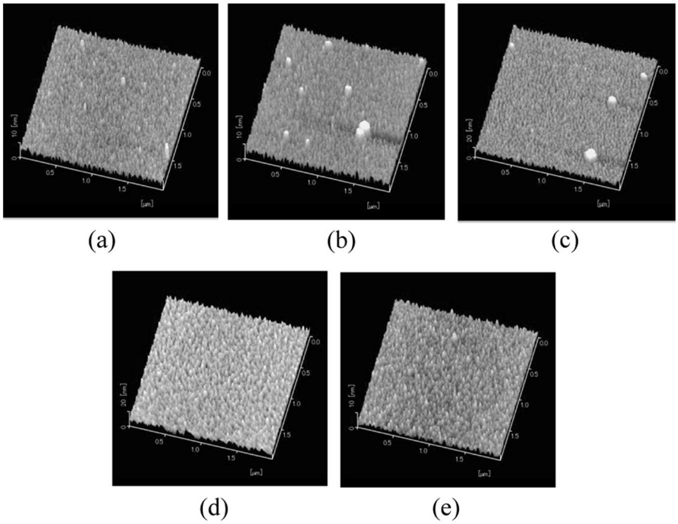
(a) (b) (c) (d)

FIGURE 3 Transfer characteristics of OFETs devices of C_{60} film on the various kinds of surface, (a) OTS, (b) HMDS, (c) *m*-MTDATA (20 nm) films, and (d) NPD (30 nm).

μ is the carrier mobility, and V_T is the threshold voltage. The performances of each device were summarized in Table 1. The conventional surface treatment by OTS and HMDS brought about high electron mobility of 0.50 and 0.80 cm^2/Vs, respectively, whereas the normal device on the non-treated substrate showed low mobility of 7.5×10^{-3} cm^2/Vs. However, it should be noted that the hetero-layered device with *m*-MTDATA and NPD achieved very high electron mobility of 1.8 and 1.8 cm^2/Vs, respectively. The improvement of mobility by

TABLE 1 OFET Performances of C_{60} Films Deposited on Various Modified Surfaces

Surface	Mobility (cm^2 V^{-1} s^{-1})	Threshold (V)	On/Off ratio
SiO_2	7.5×10^{-3}	66	6.6×10^4
OTS	5.0×10^{-1}	23	5.8×10^6
HMDS	8.0×10^{-1}	30	1.0×10^7
m-MTDATA	1.8	23	7.8×10^4
NPD	1.8	22	2.6×10^5



(a) (b) (c)

(d) (e)

FIGURE 4 The AFM images ($2 \times 2\,\mu m^2$) of C_{60} deposited film (100 nm) on the various kinds of surface, (a) non-treated SiO_2, (b) OTS, (c) HMDS, (d) *m*-MTDATA (20 nm), and (e) NPD (30 nm).

OTS or HMDS treatment is generally interpreted as elimination of surface electron traps by perfectly inert surface monolayer [12]. Therefore, we can conclude that this simple method of inserting an electronic active semiconductor layer is more efficient to reduce the electron traps than the conventional surface treatment.

The mobility improvement can be caused also by change of the film structure. We observed the morphology of the C_{60} films deposited on *m*-MTDATA and NPD interfacial layer, and those on the non-treated, OTS-treated and HMDS-treated substrates, by atomic force microscopy (AFM) as shown in Figure 4. The deposited film of C_{60} has a granular surface with a diameter around 100 nm, and almost no difference was observed for all the films. The root-mean-square (RMS) roughness of the C_{60} films on the *m*-MTDATA (1.9 nm) and NPD (1.9 nm) are almost the same with those on the non-treated substrate (1.5 nm), OTS-treated substrate (1.5 nm), and HMDS-treated substrate (2.9 nm). These results indicate that the observed improvement of electron mobility was not due to the morphological change of the C_{60} films.

Thus, the effect of the hetero-layered structure of C_{60} OFET with hole transporting material is attributed to the electronic effect at the interface. Figure 5 shows the relationship of the energy levels (the highest occupied molecular orbital (HOMO) and the lowest unoccupied

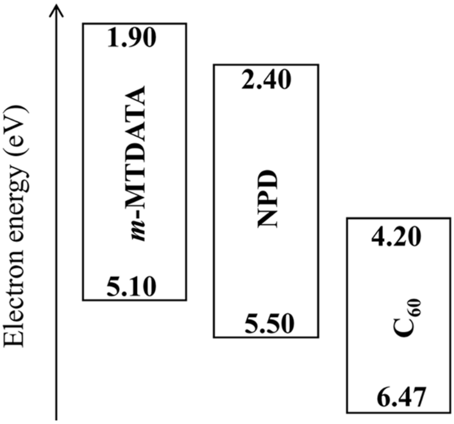


FIGURE 5 The energy levels of the organic semiconducting materials used in the hetero-layered structure OFETs.

molecular orbital (LUMO)) among the used organic semiconductors. HOMO and LUMO levels of hole transporting materials are higher than those of C_{60}. There is a large electron injection barrier from C_{60} (4.20 eV) to *m*-MTDATA (1.90 eV) or NPD (2.40 eV). Therefore, when the gate is positively biased, injected electrons from the source electrode would accumulate at the interface between C_{60} and hole transporting layer. In that case, the gate capacitance should be estimated from SiO_2 (300 nm) and hole transporting layer ($20 \sim 30$ nm). However, we cannot determine the channel interface confidently; therefore, in this study, we estimated the mobility simply assuming the gate capacitance of SiO_2. The primary effect of the interfacial layer would be isolation of channel electrons from the SiO_2 substrate surface having electron traps. This interpretation is supported by the fact that the threshold voltage becomes smaller (negatively shift) than that of non-treated device, which is similar to the effect of OTS and HMDS treatment. However, the hetero-layered OFETs with *m*-MTDATA showed higher mobility than that with OTS and HMDS treatment. This result implies some additional effects by organic semiconductor unlike merely inert insulating layer. We guess this phenomenon as follows. In the single layer device of C_{60}, there are deep electron traps in the C_{60} film itself, in addition to the SiO_2 surface. They cannot be eliminated by surface treatment of the substrates. On the other hand, the hole transporting materials have higher HOMO level and electron-donating character. Therefore, the interfacial layer tends to give electrons toward C_{60} film at the interface. It does not eliminate or reduce the electron traps, but the deep electron traps are expected to be filled in advance. As result, the injected electrons moved smoothly at the interface, resulting in the observed high electron mobility. We conclude that this trap-filling effect is essential of the hetero-layered OFET.

CONCLUSION

In summary, we demonstrated high performance C60 OFET with a hetero-layered structure including the hole transporting interfacial layer between the insulator and channel semiconductor. These results indicate that such electronic active material can be used for the interfacial layer and realizes rather better performance than the conventional inert surface treatment. These results can be interpreted as trap-filling effect of hole transporting material having electron-donating character.

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