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Ambipolar Transport in Bilayer Organic Field Effect Transistor based on Poly(3-hexylthiophene) and Fullerene derivatives

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Abstract:

Ambipolar characteristics in organic field effect transistor (FET) having bilayer structure consisting of Poly(3-hexylthiophene) (P3HT) and fullerene derivative (PCBM) are reported. P3HT was deposited by a floating film transfer method (FTM) with toluene solution on spin-coated PCBM. The FTM film found to show relative high hole mobility even casting from toluene solution. Even after coating P3HT on PCBM with FTM method, a relative high n-type transport was obtained. This indicates that the FTM method employed in this study should be mild way to coat the organic thin film on an organic semiconductor layer in terms of minimize the effect of carrier transport in the under layer. The transport characteristics have been discussed in comparison to those of ambipolar FETs prepared by other methods previously reported.

KEYWORDS: Floating film transfer method, Polythiophene, PCBM, Field effect transistor, Ambipolar transport

1. Introduction

The organic electronic devices have been extensively studied, because of their lightweight, flexible as well as low cost fabrication processes. Solution processes like roll to roll and inkjet printings has an advantage in comparison to vacuum deposition in terms of the fabrication cost. Organic materials having large carrier mobilities are required for high performance electronic devices. The carrier mobility determines the frequency response and the switching performance of field effect transistor (FET). Besides this, carrier mobility is strongly influenced by impurity and defect in the film as well as by the fabrication method and device structure [1]. Recently, hole and electron mobilities in the order of 0.1−1 cm^2/Vs in pentacene [2, 3] and C_{60} [2, 4] have been reported with vacuum deposition procedure. These mobilities are temporary satisfactory to build up active matrix displays. However, such high transport performance is still required to achieve with solution process for organic FETs. Therefore, establishment of deposition method of organic thin film having high transport performance is still highly desired.

Both of p-and n-type semiconductors are essentially required to build inverter for simple logic circuit. Organic materials have a large advantage to prepare ambipolar transport, which show both of p- and n-type transports by switching the polarity of gate bias in FET with one step deposition. In our previous report, the ambipolar FETs has been fabricated by blending poly(3-hexylthiophene) (P3HT) as p-type and fullerene derivative of [6,6]-phenyl-C61-butyric methyl ester (PCBM) as n-type semiconductors. Although this provides a very unique concept to tune both of the hole and electron transfer performance with blending ratio, a drastic drop in each mobility is a crucial problem[5, 6].

Layer structure consisted of individual p- and n-type semiconductors is one of the prospective ways to improve the transport properties in ambipolar FETs due to separate each carrier transport like a highway.

This is also correlated to the structure of the high electron mobility transistors (HEMT) established in Si FET. By way of wet-casting methodology as an eco-fitting procedure, minimizing the damage on the transport performance of under layer is the key issue for judicious employment of a solution process suitable for organic multilayer construction. As one trial to fabricate bilayer structure with solution process, the insertion of a protection layer with ethanol had been already reported.[6] Although an ambipolar transport was successfully observed with this method, a large decrease of transport performance in under layer was found. To improve the high performance of ambipolar transport, the development of other solution deposition method to fabricate bilayer ambipolar FET was still required.

A novel technique of floating film transfer method (FTM) of P3HT layer has been developed to fabricate a thin cast-film on a liquid substrate.[7] The FTM is a similar method to deposition thin film with Langmuir Blodgett (LB) method.[8, 9] Although LB film is sophisticated technique using highly controlled conditions, the FTM method offers a relatively simple procedure without any surface pressure. FTM technique possibly fabricates organic bilayer films without spoiling the bottom layer seriously. The morphology of P3HT film obtained by FTM technique also demonstrated a well-ordered structure compared with that of spin-coated film.[7]

In this paper, the ambipolar transport characteristics in bilayer FET consisting of PCBM and P3HT with FTM method are reported in comparison to the transport characteristics of ambipolar FETs. A newly configured device structure for ambipolar transport was also proposed. The change of transport characteristics has been discussed in terms of the device configuration as well as transport performance of p- and n-type materials.

2. Experimental

P3HT and PCBM were used as obtained from Merck (Iliscon SP100) and Frontier Carbon (nanom spectra E100H), respectively. Silicon wafer having an oxide layer with thickness of 300 nm (Si/SiO_2) was employed as the substrate for all the FETs in this study. The SiO_2 surface was hydrophobitized with silanizing agents such as hexamethyldisilazane (HMDS), Octyltrichlorosilane (OTS) and Octadecyltrichlorosilane (ODTS) [10]. The effects of surface treatments of Si/SiO_2 on the n-type transport characteristics of PCBM FET were also investigated to optimize the device performance.

PCBM FETs were fabricated by spin coating of 1wt % chloroform solution at 6000 rpm for 10 s on a substrate. The thicknesses of PCBM films were typically estimated to be 20nm by DEKTAK 6M Profiler. Au electrodes and a LiF interlayer were deposited to form the top contact on the PCBM layer under vacuum at 6×10^{-6} Torr. The thickness of Au and LiF were typically 50 nm and 1nm, respectively. Source and drain electrodes were patterned by the physical vapor deposition of gold using shadow masking technique. The fabricated channel length (*L*) and width (*W*) of FET were 20 μm and 2.0 mm, respectively.

The device structure of bilayer FET employed in this study is shown in Fig.1. Upper P3HT layer was prepared by FTM technique on a PCBM FET as shown in Fig.2. For depositing FTM film, a 1wt% toluene solution of P3HT was dropped on an ethylene glycol. The drop of P3HT was spread out instantly into a very thin film on the surface of ethylene glycol. Toluene being lighter and immiscible to ethylene glycol, the floating solution on the surface leads to the formation of a well-stacked and smooth thin film on the ethylene glycol surface. The film was then transferred onto a substrate. The FTM technique resulted to deposit a P3HT film typically in the thickness of 20nm. Thus, FTM eliminates the need for any sophisticated procedures, also at the same time the resulting films possess high degree of lamellar structure

similar to that of casted films, although their thickness is comparable to that of spin-coated ones. The unique combination of these features makes FTM highly lucrative procedure for fabricating thin film transistors. The device was heated at 80˚C, for 15 min under dried nitrogen atmosphere in order to remove the solvent and to anneal the P3HT.[11, 12)] Single layer P3HT FET was also fabricated by the FTM technique to investigate the transport characteristics.

All of the electronic characteristics were measured by a Keithley 2612 two channel electrometer in vacuum at 10^{-6} Torr. The field-effect mobility (μ) as well at the threshold voltage was estimated with transfer characteristics according with the conventional methodology.[5-6, 13)] The double-layer formation was confirmed by the thickness measurement at the channel area by comparing before and after the upper layer deposition. The film surface morphology was also observed by Atomic Force Microscope (AFM) measurement. AFM image is captured with tapping mode by a JEOL AFM model JSPM-5200.

3. Results and Discussion

Uniform FTM films were formed on ethylene grycol surface. The area of FTM films was almost reached to be around 4–6cm in a 9cm size petridish. The FTM method is one of the casting procedures to provide extra-thin hydrophobic film with large area. The P3HT FTM film could be well transferred on a hydrophobic SiO_2 surface as smooth layer. Instead of P3HT, poly-9,9'-dioctyl-fluorene (PFO) was also tried to use for making a FTM film, which forms a strong freestanding thin film. The finding mechanical toughness indicates the FMT film being to form well-stacked film suitable for transverse transport and for flexible electronics.

Figure 3 shows an AFM image of P3HT FTM film fabricated from 1wt% toluene solution.

Squamiform structure, around 5 nm thick with 50 nm long, was observed in this image. Besides this, spin-coated films were reported to show relative flat surface mainly consisted with amorphous region. The image obtained above indicates the FTM film possesses rather rough surface. Related to this, the FTM film was found to be consisted of well-grown domains in our recent report.[7)] The unique rough-surface structure, therefore, possibly represents a sort of grain growth suitable for carrier transport.

Figure 4 shows typical transfer characteristics of PCBM FET with OTS surface and with LiF buffer layer. A fine n-type transport with relative large on-current and on/off ratio over than 5 orders was obtained. FET parameters such as electron mobility, threshold voltage and on/off ratio in PCBM FET are listed in Table I with different surface treatment as well as with/without LiF buffer layer underneath the Au electrode. It should be noted that the electron mobility was increased in 2 orders of magnitude by insertion of LiF layer. This is attributed to the contact level modification with LiF insertion by reducing the barrier height for electron injection from Au to PCBM[14-18)]. The hydrophobic treatment of Si/SiO_2 surface with OTS or ODTS was also provide a remarkable increase of on/off ratio attributed to the suppression of off current. The quenching of dangling hydroxyl groups on the Si/SiO_2 surface might cause to decrease the persistent off current. In this study, the surface treatment with OTS and ODTS provides better FET performance as compared to HMDS treatment for PCBM FET. Therefore, the device configuration of #4 was employed for PCBM layer fabrication in this study.

Figure 5 shows electronic characteristics of P3HT FET with FTM film. A clear p-type transfer characteristic was obtained in FTM film in particular with small hysteresis. This indicates that no obvious residual effect both of ethylene glycol and toluene was found on FET characteristics in FTM film. The FET parameters were compared in Table II. Relative high hole mobility was found in FTM film even using toluene as solvent.[5,6)]. Highly alignment of polymer chain will generate a good transport performance of

semiconducting polymers with FTM method.[apex] Guangming et. al., have demonstrated the improvement of film morphology in P3HT thin films by dip coating and casting procedures.[12,19] They argued that the longer time duration for the aggregation leads to improved alignment of polymer chains, and hence their crystallinity. The FTM method can be categorized as one deposition method to generate large-area cast film to withdraw the high performance of carrier transport in π-conjugated polymers according with gradual evaporation. The detail studies on structural and on electronic characteristics in FTM film of semiconducting polymers possibly elucidates the intrinsic transport performance of organic semiconductors.

Figure 6 shows typical output characteristics of an ambipolar P3HT/PCBM bilayer FET prepared by FTM method in (a) hole and in (b) electron dominated bias regions. Even in bilayer films, a relative small hysteresis was only observed in the electronic characteristics as also been reported in our previous reports.[5] Linear regime was only observed in hole transport at V_{DS} = −50 V. On the contrary, the electron transfer at V_{DS} = +50 V showed a clear saturation regime as seen in Fig. 6 (b). The observed output characteristics are correlated to the difference of the threshold voltage and the mobility of each transport layer. Even coating a FTM film of P3HT on PCBM layer, the n-type layer displays high electron transport characteristics.

It should be noted that the different configuration of bilayer FETs without LiF layer or with top-contact Au electrodes on the P3HT layer only displayed hole transport characteristics (results are not shown here). As already discussed above, the insertion of LiF layer is indispensable for high-performance electron transport with Au electrode for PCBM FET. Therefore, the finding hole transports are consistent to the device structure employed. The asymmetric electrode configuration shown in Fig.2 has an advantage to inject each carrier into each transport layer.

Figure 7 show transfer characteristics at (a) V_{DS} = −50 V and (b) +50 V in a bilayer FET. A relative small hysteresis was only observed with less residual effect in bilayer structure.[20] Although a clear n-type transport was observed in positive bias regime, the p-type transport is not so much clear than that of the n-type one. One reason will be attributed to the relative high mobility of n-type material as compared to the hole mobility. Besides this, the p-type transport was evaluated as bottom-contact FET with a thick gate-insulator consisted of both PCBM layer and SiO2 insulator for P3HT channel in this structure. This is also another reason to decrease the hole transport performance. Besides this, the PCBM film deposited by way of FTM from toluene failed to operate as FET so far, which prevents one from switching PCBM and PHT layers sequence. The double layer structure investigated in this study, therefore, provides the best performance of ambipolar transport at present stage.

Electron and hole mobilities, and threshold voltages in ambipolar FET consisted of P3HT and PCBM with various deposition methods are summarized in Table II with our previous reports.[5, 6] The largest electron mobility was obtained in the pristine PCBM, which clearly decreased in ambipolar FETs. Although some differences in batch of products was one factor to affect the transport performance in particular in terms of molecular weight as well as polydispersive index of P3HT.[21-23] There are other factors possibly to decrease the mobility in ambipolar FET. As also reported in the literature,[5] an essential decrease both of hole and electron transports was found in ambipolar FET consisted of blended channel. The substantial reduction of occupied volume by one material as well as the extension of transport path in the channel region should be another reason for this decrease.

Separation of hole and electron transport into individual layer possibly increases transport performance of ambipolar FET for establishing carrier transport highway. The bilayer film of PCBM on P3HT with successive spin coating of chloroform solutions with coating a ethanol protection inter-layer

employed in our previous report, however, showed large decrease at around 2 orders for the hole mobility.[6) It is explained that the insertion of ethanol layer is not effective to protect under-layer, or rather provides carrier traps for P3HT. The minimum decrease of hole and electron mobilities within one order of magnitude was found in the bilayer FET with FTM method as listed in Table II. This is therefore the best way to construct ambipolar FET consisted of two organic materials at present stage, which is possibly applicative to light emitting organic FET also. The revealed persistent decrease of the mobility still requires more detail discussion with taking an intrinsic perturbation to each transport layer at contact interface into account. The FTM method proposed in this study is possibly extended to other multilayered organic devices as a new solution process.

4. Conclusion

The present study demonstrates a new thin-film fabrication technique, floating film transfer method (FTM), on the organic-semiconductor channel of ambipolar field-effect transistor (FET). A unique device configuration of ambipolar FET with bilayer structure has been proposed. The carrier mobility was found to be superior over those in the literature. The FTM method is suitable in particular for preparation of bilayer structure in terms of minimizing the effect of carrier transport of under layer. The finding essential decrease of transport is still one issue to clarify the mechanism.

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Sports, Science and Technology, Japan.

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Table I. FET parameters using PCBM as channel with various electrodes and surface treatments.

device configuration			Electron mobility	Threshold voltage	on/off ratio
entry #	silanization	electrode	μ [cm^2/Vs]	V_{th} [V]	
1	HMDS	Au	6.0×10^{-6}	--	2.3
2	HMDS	LiF / Au	1.5×10^{-3}	35	1.3×10^{2}
3	OTS	Au	1.0×10^{-4}	-9	1.6
4	OTS	LiF / Au	8.6×10^{-2}	40	1.6×10^{5}
5	ODTS	LiF / Au	4.6×10^{-2}	38	1.5×10^{5}

Table II. Comparison of field-effect mobility and threshold voltage of ambipolar FETs consisted of P3HT and PCBM.

		This study (P3HT on PCBM)		Bilayer channel [6] (PCBM on P3HT)		Blended channel [5] (P3HT:PCBM = 1:2)	
		μ [cm^2/Vs]	V_{th} [V]	μ [cm^2/Vs]	V_{th} [V]	μ [cm^2/Vs]	V_{th} [V]
Pristine	P3HT	5.3×10^{-3}	10	8.0×10^{-4}	−16	1.4×10^{-3}	6
	PCBM	8.6×10^{-2}	40	1.1×10^{-2}	59	1.2×10^{-2}	22
Ambipolar	Hole	3.3×10^{-5}	45–74	3.6×10^{-8}	−28	5.0×10^{-5}	−12
	Electron	1.5×10^{-3}	29	1.1×10^{-5}	26	2.5×10^{-4}	10

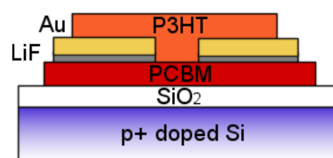

Fig.1. Device configuration of bilayer FET consisted of P3HT and PCBM with asymmetric electrode.

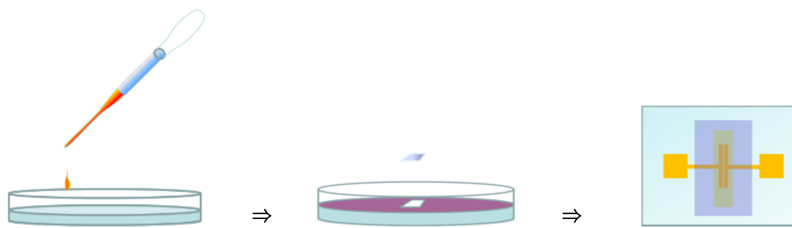

Fig.2. Procedure of floating film transfer method (FTM). Ethylene glycol was used as deposition substrate. 1wt% toluene solution was used as P3HT solution in this study.

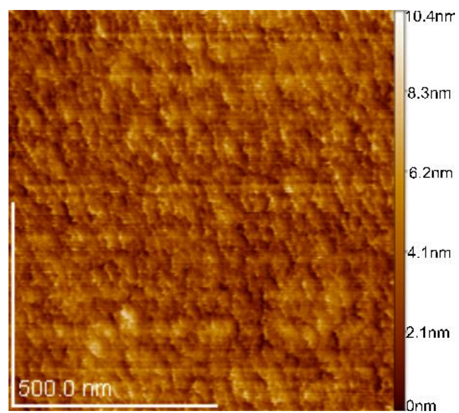

Fig.3. Tapping mode AFM image of P3HT FTM film.

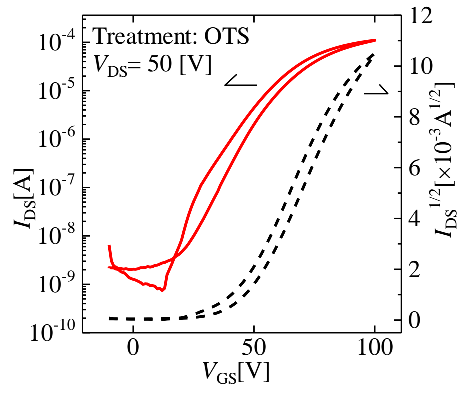

Fig.4. Transfer characteristics of PCBM single layer FET with top contact Au/LiF electrode and OTS dielectric surface.

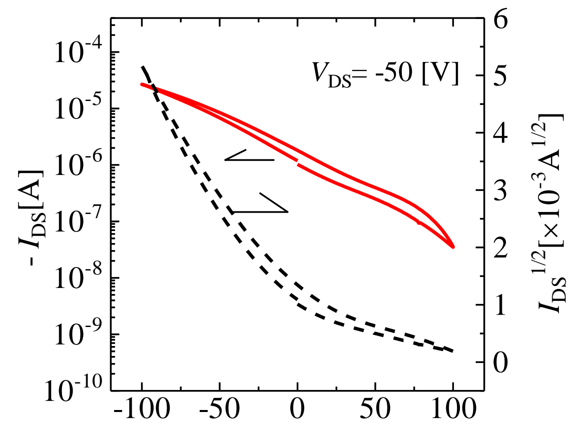

Fig.5. Transfer characteristics of P3HT FETs with Au bottom contact fabricated by FTM technique.

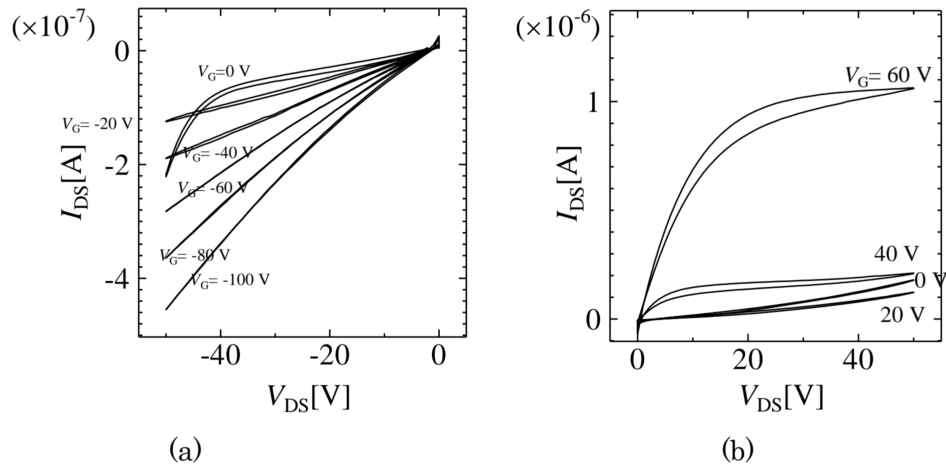

Fig.6. Output characteristics of ambipolar bilayer FET biased under (a) hole-transport dominated and (b) electron-transport dominated regions, respectively.

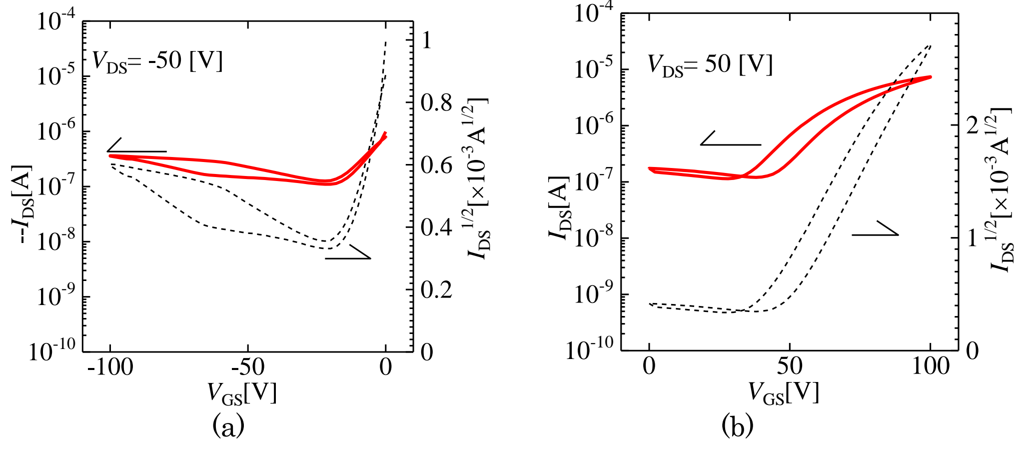

Fig.7. Transfer characteristics of ambipolar bilayer FET at (a) V_{DS} = −50 V and at (b) V_{DS} = +50 V, respectively