

Depletion- and ambipolar-mode field-effect transistors based on the organic heterojunction composed of pentacene and hexadecafluorophthalocyaninatocopper

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ABSTRACT

We investigated heterojunction organic field-effect transistors (OFETs) using pentacene and hexadecafluorophthalocyaninatocopper ($F_{16}CuPc$) as double active layers. Two operation modes including depletion- and ambipolar-type were observed depending on the deposition order of two organic films. Depletion-mode was firstly observed from that devices with pentacene as the bottom layer and $F_{16}CuPc$ as the top layer, which was attributed to dipole effects originated from the pentacene/ $F_{16}CuPc$ interface. Then improved device performances were obtained with mobility from 0.87 to 1.06 cm^2/Vs , and threshold voltage shifted from -20 to $+25$ V as compared with conventional pentacene-based devices. Furthermore, the heterojunction OFETs exhibited typical ambipolar transport when alternating the deposition order of two films, which exhibited ambipolar mobilities with 0.06 cm^2/Vs for electron and 0.0025 cm^2/Vs for hole, respectively. All results implied the utilization of heterojunction can effectively improve the device performances of OFET, and operation mode strongly on the deposition order of two films.

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1. Introduction

Organic field-effect transistors (OFETs) have been widely studied due to their potential applications in flat-panel display, low-end storage elements, sensors and complement circuits [1–4]. In past a few years, organic heterojunction has been introduced to OFETs in order to realize ambipolar devices [3,5–9]. The motivation of ambipolar OFETs is based on the necessity of simple fabrication complementary inverters like complementary metal-oxide-semiconductors (CMOS). It is well known that complementary technology will bring several advantages including better noise margin, lower power dissipation, and simplifying process [10]. One promised approach for achieving this goal is using ambipolar devices as fabricated elements. It is well known that ambipolar devices possess simultaneously both n- and p-type transport capability and thus reducing a step of patterning organic semiconductor, at the same time it can be operated for both positive and negative voltage unlike conventional unipolar devices that only operated for one polarity. However, the electric characteristics of ambipolar transistors are still worse than that of single-layer devices. Therefore, the studies on organic heterojunction are crucial for high-performance ambipolar OFETs.

Up till date, various process technologies for ambipolar OFETs have emerged by the combination of two organic components [11], the modification of metallic electrodes [12], using narrow band-gap materials [13], and utilizing organic heterojunction [6]. Among these methods, organic heterojunction is mostly popular for easily realizing ambipolar transportation. Actually, the first ambipolar OFET in the world was realized by employing organic heterojunction consisting of $C_{60}/6T$ in 1995 by Dodabalapur et al. [5]. Up till now, several organic heterojunction pairs have been reported including $C_{60}/pentacene$ [7], $CuPc/F_{16}CuPc$ [8], $BP2T/F_{16}CuPc$ [9], $PTCDI-C_{13}H_{27}/pentacene$ [14], $PCBM/PPV$ [15], etc. The highest field-effect mobilities reached up to 0.23 cm^2/Vs for electron and 0.14 cm^2/Vs for hole based on $C_{60}/pentacene$ heterostructure in inert ambient.

In this paper, the heterojunction OFETs consisting of n-type hexadecafluorophthalocyaninatocopper ($F_{16}CuPc$) and p-type pentacene have been studied for the following reasons. Pentacene, one of well-studied p-type semiconductor, shows the highest field-effect mobility [16] among all organic semiconductors. The n-type semiconductor, $F_{16}CuPc$, also shows high carrier mobility [17] and excellent stability in air, which offers enough flexibility for fabrication and measurement. Although pentacene and $F_{16}CuPc$ have different molecular shape and crystal packing manner (Fig. 1(a and b)), pentacene/ $F_{16}CuPc$ heterojunction transistor can realize high device performances and typical ambipolar transport by proper deposition processes. OFETs with two operation modes

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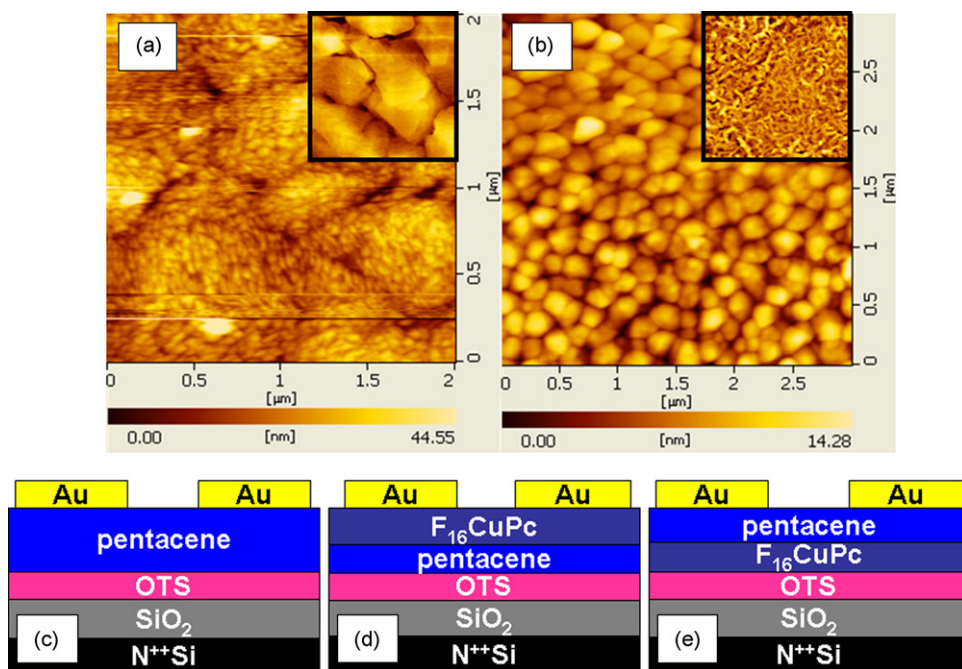


Fig. 1. AFM image (a) 15 nm $F_{16}CuPc$ on 10 nm pentacene; (b) 15 nm pentacene on 7 nm $F_{16}CuPc$ the inserts are pentacene (a) and $F_{16}CuPc$ (b) on OTS/ SiO_2 ; (c) schematic diagram of OFET with top contact based on pentacene as the active layers; (d) schematic diagram of OFET with top contact based on pentacene/ $F_{16}CuPc$ heterojunction as the active layers; (e) schematic diagram of OFET with top contact based on $F_{16}CuPc$ /pentacene heterojunction as the active layers.

were demonstrated depending on the deposition order of two films that resulted in different interfaces for charge accumulation.

2. Experimental

Fig. 1(c–e) shows three structures of single-layer pentacene, pentacene/ $F_{16}CuPc$, and $F_{16}CuPc$ /pentacene heterojunction OFETs, respectively. All devices were fabricated on the substrate of heavily doped silicon wafers ($0.01\text{--}0.015\ \Omega\text{ cm}$) served as gate electrode. A layer of oxide (SiO_2) covered on the substrate acted as gate insulator by thermal growth. Then, the SiO_2 was modified with octyltrichlorosilane (OTS) solution for the optimization of surface properties [18]. These wafers were immersed to OTS solution (chloroform as solvent, 2 mM) for 1 day and rinsed three times by solvent to remove aggregated OTS particles. The capacitance of SiO_2 /OTS (8 nF/cm^2) was measured with an Agilent E 4980A LCR meter. The pentacene and/or $F_{16}CuPc$ used as active layer were successively deposited onto the wafers by vacuum sublimation at a fixed rate of 0.1 nm/s (it is recorded by quartz oscillate) under background pressure of 10^{-4} Pa . At the same time substrate temperatures were set at 120°C for $F_{16}CuPc$ and 70°C for pentacene film, respectively. All organic chemicals were purchased from Aldrich Company. Finally, 40 nm Au source/drain electrodes were deposited through shadow mask by thermal evaporation, where defined channel width (W) and length (L) was $3800\ \mu\text{m}$ and $180\ \mu\text{m}$, respectively. Device performances were measured by Agilent 4155C semiconductor analyzer at room temperature in air ambient. The atomic force microscopy (AFM) images were performed by SPI 400 with tapping mode.

3. Results and discussion

We first investigated the electrical characteristics of pentacene/ $F_{16}CuPc$ heterojunction (pentacene as the bottom layer and $F_{16}CuPc$ act as the top layer) transistor (Fig. 1(d)) in contrast to that of pentacene-based single-layer device (Fig. 1(c)).

Typical output curves of the pentacene/ $F_{16}CuPc$ heterojunction (pentacene (10 nm) and $F_{16}CuPc$ (15 nm)) OFETs are shown in Fig. 2(a). The linear and saturation regions can be observed with the increase of drain-source voltage (V_D). It shows a typical p-channel field-effect transistor characteristic. For comparison, the output curves of pentacene single-layer device are also presented in Fig. 2(a). At $V_G = -50\text{ V}$ and $V_D = -50\text{ V}$, the on-state current (I_{on}) is $265\ \mu\text{A}$ for heterojunction transistor, and $50\ \mu\text{A}$ for pentacene single-layer device, it implied that a five-fold increased current has been obtained. Furthermore, off-state current defined as $V_G = 0\text{ V}$, is about $10^{-12}\text{--}10^{-10}\text{ A}$ for single-layer device, while 10^{-5} A for the heterojunction device that meant depletion operation mode has been exhibited.

The field-effect mobilities and threshold voltage were extracted from saturation region based on the transfer curves using the follow equation:

$$I_D = \frac{W}{2L} C_i \mu (V_G - V_T)^2 \quad (1)$$

where W and L are the width and length of the channel, C_i is the capacitance of the gate insulator; μ is the field-effect mobility, and V_T is the threshold voltage. Fig. 2(b) shows the transfer characteristics of pentacene/ $F_{16}CuPc$ heterojunction transistor and pentacene single-layer device. The V_G are applied from +100 to -50 V with a fixed V_D of -50 V . The depletion and accumulation processes of hole may be found by scanning V_G from positive to negative value. The field-effect mobility of pentacene/ $F_{16}CuPc$ heterojunction OFET extracted from Fig. 2(b) is $1.06\text{ cm}^2/\text{Vs}$, which is higher than that of pentacene single-layer device ($0.87\text{ cm}^2/\text{Vs}$). This indicates that the introduction of heterojunction can enhance effectively charge injection efficiency. In addition, a large shift of threshold voltage is observed from -20 to $+25\text{ V}$, which implies that operation mode has been transformed from accumulation-mode for single-layer OFET to depletion-mode for pentacene/ $F_{16}CuPc$ heterojunction transistor. Therefore it can be deduced that the conductive channel has been formed in heterojunction transis-

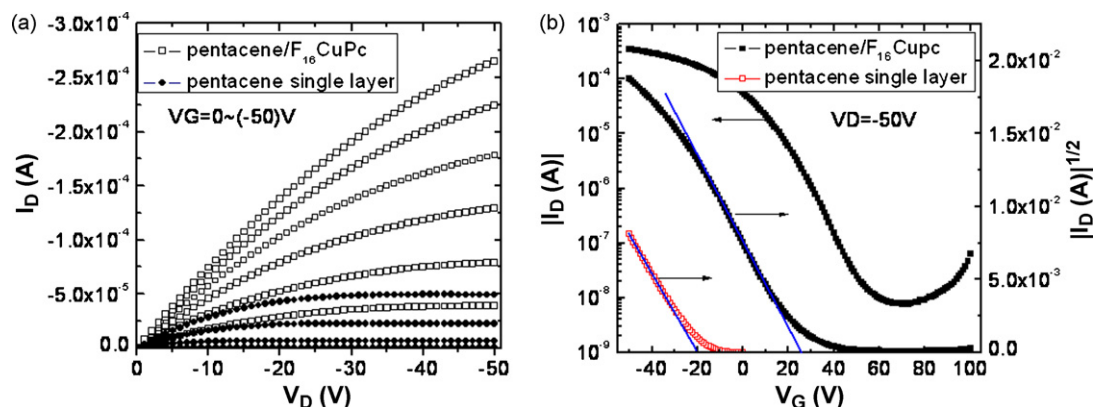


Fig. 2. (a) The two output characteristics for pentacene/ F_{16} CuPc heterojunction OFET and pentacene single-layer OFET; (b) $|I_D|^{1/2}$ vs. V_G characteristics for single pentacene OFET and pentacene/ F_{16} CuPc heterojunction OFET (together with the plot of $|I_D|$ vs. V_G).

tors even though $V_G = 0$ V. It is worth mentioning that in the case the on/off ratio can still reach up to 10^5 due to high on-state current. Therefore, high-performance, depletion-mode, p-channel organic field-effect transistors have been realized by using the pentacene/ F_{16} CuPc heterojunction structure. However there is still no ambipolar phenomenon that can be observed in this heterojunction transistor.

In order to make the conductive mechanism clear, we depict energy level schemes shown in Fig. 3(a and b). The energy levels of pentacene and F_{16} CuPc were obtained from Refs. [7,19]. The highest occupied molecular orbital (HOMO) level of pentacene lies at 5.0 eV and the lowest unoccupied molecular orbital (LUMO) level of F_{16} CuPc is 4.8 eV, as shown in Fig. 3(a). It is noted that the intrinsic Fermi level of pentacene is higher than that of F_{16} CuPc. Therefore, when pentacene and F_{16} CuPc are brought together into contact, energy level will induce to bend, the HOMO of pentacene bends upwards whereas the LUMO of F_{16} CuPc bends downwards (Fig. 3(b)). Carrier, electrons in F_{16} CuPc and holes in pentacene, are accumulated at both sides of the heterojunction interface (Fig. 3(c)). This accumulation effect may be caused by charge transfer from pentacene to F_{16} CuPc, thus a polarized layer formed at the heterointerface. Similar phenomena have been also observed in the system of ZnPc/ F_{16} ZnPc, which results in interface dipole by analyzing UPS spectra and molecular orbit calculation [20]. Therefore, there existed a conductive channel formed by inducing electrons and holes at the heterointerface.

From the above analysis, both electron and hole currents made a contribution to the high conductivity of heterojunction OFETs. However, only dominated hole current was observed in

pentacene/ F_{16} CuPc heterojunction transistors. We can explain this phenomenon by AFM images. When F_{16} CuPc grown on the SiO_2/OTS , thin-film image displayed strip grains with larger size (200 nm), as shown in Fig. 1(b). The morphology of F_{16} CuPc turned to like dot scope with smaller grain size (90 nm, shown in Fig. 1(a)) when grown on the pentacene substrate, which resulted in the decrease of carriers transport including smaller carrier mobility and higher threshold voltage. In this condition, electron transport channel was difficult to form so that pentacene/ F_{16} CuPc heterojunction transistors showed hole-only transport.

For further obtaining ambipolar transport characteristics, we altered the deposition order of two films, F_{16} CuPc was used as the bottom layer and pentacene as top layer. The device structure is shown in Fig. 1(e). Thus, holes can be efficiently injected into the HOMO level (5.0 eV) of pentacene from Au (work function: ~ 5.1 eV [21].) and form accumulation layer at the pentacene/ F_{16} CuPc interface. On the other hand, the electrons are injected from HOMO level of pentacene into the LUMO level of F_{16} CuPc to form the electron accumulation layer at the F_{16} CuPc/ OTS interface.

Fig. 4(a) shows drain current (I_D) vs. drain voltage (V_D) characteristics of the heterojunction transistor. The device exhibits an apparent ambipolar transport behavior at a $V_G > |20|$ V. I_D increases with the magnitude of V_D , with transition from linear regime to saturation regime, and becomes larger at higher V_G . However, in the region of low V_G and high V_D , I_D increases superlinearly with V_D , and becomes smaller at higher V_G . This phenomenon is similar to that of pentacene/ C_{60} heterojunction transistor [7]. Fig. 4(b) represents the corresponding plots of $|I_D|^{1/2}$ as a function of V_G for the F_{16} CuPc/pentacene heterojunction transistor. The threshold voltage (V_T) and carrier mobility can be extracted from the curve. The device exhibit strong field-effect modulation of channel conductance in the ambipolar operation with a V_T of 8 V for n-type and a V_T of 30 V and p-type operation, respectively. Then the ambipolar field-effect mobilities were estimated to be 0.06 and $0.0025 \text{ cm}^2/\text{Vs}$ for the n- and p-channel, respectively. Note that the hole mobility of F_{16} CuPc/pentacene heterojunction transistor is lower than that of pentacene single-layer device. This can also be explained by the AFM image that the grain size of pentacene film deposited on SiO_2/OTS substrate is much smaller than that of deposited on F_{16} CuPc substrate, as shown in Fig. 1(a and b). Therefore, it results in the drop of hole mobility due to the increased grain boundary. Additional, there may have many hole-traps on the F_{16} CuPc surface, and this may also cause to low carrier mobility. More importantly, these ambipolar devices exhibit excellent air-stability that no apparent change on the device performance was observed by exposing them to air for about three months. As a result, an ambipolar OFET having excellent air-stability has been demonstrated based on F_{16} CuPc/pentacene heterojunction.

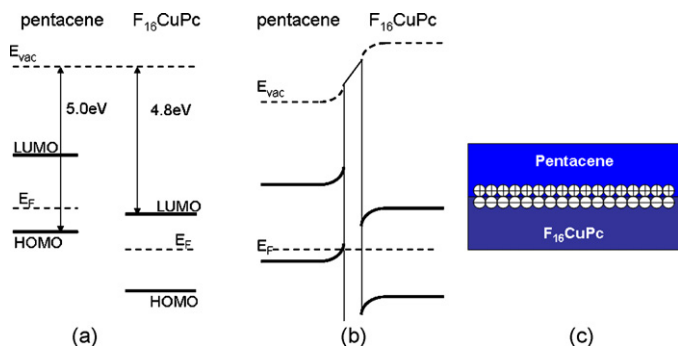


Fig. 3. (a) Energy diagram of pentacene and F_{16} CuPc before (a) and after (b) contact. E_{vac} and E_F denote the vacuum level and Fermi level, respectively. (c) The charge carrier distribution at the heterojunction of pentacene and F_{16} CuPc under zero bias conditions.

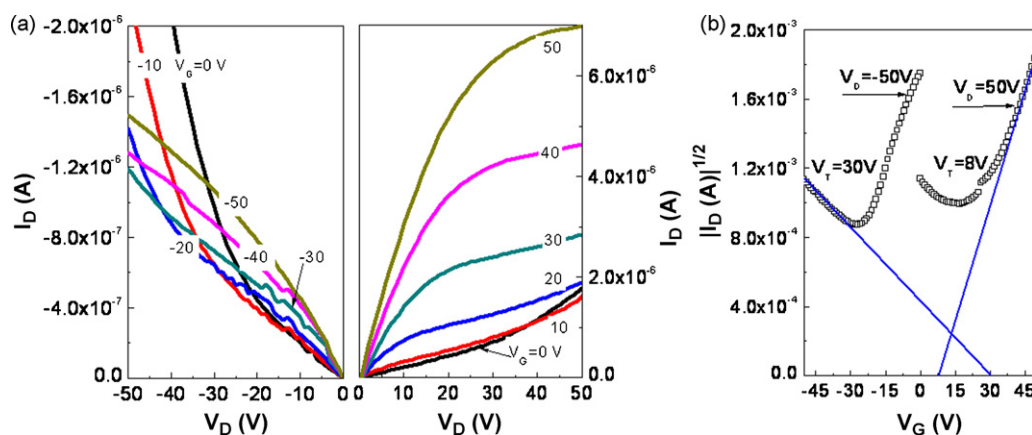


Fig. 4. (a) Output curves for the p- and n-channel regimes of the $F_{16}CuPc$ /pentacene heterojunction ambipolar OFET (V_G ranging from 0 to ± 50 V at a step of ± 10 V); (b) $|I_D|^{1/2}$ vs. V_G characteristics at fixed $|V_D|$ of 50 V for the $F_{16}CuPc$ /pentacene heterojunction OFET.

4. Conclusion

We have described the behavior of charge transport in organic heterojunction comprising of n-type $F_{16}CuPc$ and p-type pentacene. The HOMO of pentacene bends upwards and the LUMO of $F_{16}CuPc$ bends downwards since the electrons and holes are accumulated at both sides of the organic heterojunction interface, which induce to an interface dipole. OFETs based on pentacene/ $F_{16}CuPc$ can be operated in depletion-accumulation-mode. The field-effect mobility of $1.06 \text{ cm}^2/\text{Vs}$ is significantly higher than that of $0.87 \text{ cm}^2/\text{Vs}$ of pentacene single-layer device, and the threshold voltage shifts from -20 to $+25$ V. Furthermore, ambipolar conduction behavior is observed for $F_{16}CuPc$ /pentacene heterojunction OFETs. The electron and hole mobilities are 0.06 and $0.0025 \text{ cm}^2/\text{Vs}$, respectively. The studies of electric charges conduction mechanism in organic heterojunction are helpful for the development of organic field-effect devices.

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