High-performance n-channel organic thin-film transistors based on the dual effects of heterojunction and surface modification*

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This paper presents two n-channel organic heterojunction transistors with modified insulator by using hexadecafluorophthalocyaninatocopper (F_{16}CuPc)/copper phthalocyanine (CuPc) and F_{16}CuPc/pentacene as the active layers. Compared with a single-layer device, it reports that an improved field-effect mobility and a 6-fold higher drain current are observed. The highest mobility of 0.081 $cm^2/(V \cdot s)$ was obtained from F_{16}CuPc/CuPc heterojunction devices. This result is attributed to the dual effects of the organic heterojunction and interface modification. Furthermore, for two heterojunction devices, the performance of the F_{16}CuPc/CuPc-based transistor is better than that of F_{16}CuPc/pentacene. This is attributed to the morphologic match of two organic components.

Keywords: n-channel, heterojunction effect, surface modification

PACC: 7120H, 7125V, 7340L, 7360P

1. Introduction

Organic complementary logic circuits are of great interests due to their potential applications in low-cost, large-area flexible electronics.[1] Complementary technology displays several advantages including low power dissipation, a high robustness, and a good noise margin.[2] A complementary circuit may be realized by integrating an n-channel and a p-channel organic thin-film transistor (OTFT). However, n-channel OTFTs often exhibit low field-effect mobility and poor stability in comparison with these p-channel devices. This has been a bottleneck and limits the development of complementary technology. Up to now, the highest mobility of 6.0 $cm^2/(V \cdot s)$ has been obtained from C60-based transistors.[3] However, most n-channel TFTs exhibit characteristics only in the ambience of inert gas or vacuum, because ambient oxygen or moisture can act as electron traps[4,5] which implies the instability of the devices in air. Therefore, a high-performance and air-stable n-channel OTFT is desired.

It is well known that high-performance OTFTs originated from both excellent materials and elaborate device design. The key factors related to device architecture still concern two interfaces including organic semiconductor and source/drain, organic semiconductor and gate insulator. Actually, n-channel devices suffer more from these interfaces than p-channel devices.[6] However, from this viewpoint, correlative studies are still rare.

In this paper, we investigate the interface conditions of n-channel devices by using different materials to achieve high-performance. A promising n-type material, hexadecafluorophthalocyaninatocopper (F_{16}CuPc) has high air stability and an electron field-effect mobility of ca. 0.03 $cm^2/(V \cdot s)$.[7,8] It can exclude the effects of air by F-bond. We herein expect to improve the performances of F_{16}CuPc-based TFT by elaborate device configuration. The dual effects of organic heterojunction and insulator-modification are introduced to optimize two key interfaces of the above mentioned OTF. Classic p-type semiconductor pentacene and copper phthalocyanine

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(CuPc) are selected to form a heterojunction with F_{16}CuPc. Octadecyltrichlorosilane (OTS) is used as a typical interface modification reagent to active gate insulator by self-assembly monolayer (SAM) technology.

2. Experimental

Figure 1 shows the device structure of heterojunction OTFTs using conventional top-contact configuration.[9] All devices were fabricated on the substrate of a heavily doped silicon wafer (0.01–0.015 $\Omega \cdot$cm) as well as gate electrode. The OTS thin film acts as the modified layer covered on the surface of SiO_2 by inserting the substrate to OTS solution (chloroform as solvent, 2×10^{-3} mol/L) for 1 day. The SiO_2/OTS was used as gate insulator with a capacitance of 8 nF/cm^2. The F_{16}CuPc was used as the bottom layer, and the CuPc or pentacene as the upper layer. For improving the electric characteristics of OTFTs, the substrate temperatures were held at 125 °C due to morphological reasons.[10] Organic thin films were deposited by vacuum deposition at a fixed rate of 1 nm/s (this is recorded by the oscillation of the quartz crystal) at a substrate temperature of 125 °C under a background pressure of 10^{-4} Pa level. The thickness of F_{16}CuPc, CuPc and Pentacene was held carefully at a constant of 10 nm. Organic chemicals were purchased from Aldrich Company without purification before use. Finally, 30 nm Au source/drain electrodes were deposited through a shadow mask by thermal evaporation, whose defined channel width (W) and length (L) were 1250 and 90 μm, respectively. The device performance was recorded by an Agilent 4155C semiconductor analyser at room temperature in air ambience. The morphology of the deposited organic layers was examined by atomic force microscopy (AFM) with SPA-400 SPM UNIT (Seiko Instruments Inc.).

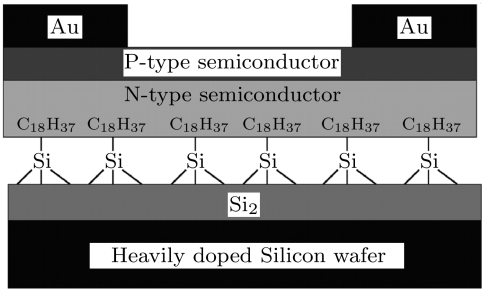


Fig. 1. Schematic diagram of n-channel heterojunction OTFTs based on a modified insulator.

3. Results and discussion

3.1. Single-layer F_{16}CuPc TFT

Figure 2(a) shows two output characteristics of F_{16}CuPc transistors with bare SiO_2 and SiO_2/OTS substrate, respectively. A typical TFT current in the linear and saturation regions can be seen clearly from it. The field-effect mobility in the saturation region was extracted from transfer characteristics shown in Fig. 2(b) by using the equation $I_{\rm D} = (W/2L)C_{\rm i}\mu(V_{\rm G} - V_{\rm T})^2$. The mobility from the bare SiO_2 substrate-based device is 0.028 cm^2/(V$\cdot$s). The other from the device with SiO_2/OTS substrate is 0.048 cm^2/(V$\cdot$s). Both of the two devices exhibit a threshold voltage of approximately 20 V. From these results, an improvement of device performance was obtained, which implies that the introduction of the OTS modified layer is very useful for OTFT.

In previous work, OTS has been applied widely to optimize the electric characteristics of OTFT. Its functions include improving the morphology of organic film, changing the surface energy of inorganic oxide, and lowering the leakage current of devices.[11,12] In 2005, Cambridge's research group proposed that the OTS might eliminate the electron traps brought by the OH- group on the surface of SiO_2, which could link an alkyl group to SiO_2 by forming a monolayer of self-assembly, shown in Fig. 1.[13] Here, three reasons may be responsible for the improvement in our study. Firstly, OTS acts as a bridge linking the inorganic dielectric and organic semiconductor. It optimizes the surface energy of SiO_2 which increases the adhesion of the organic semiconductor on the substrate.

An AFM image of F_{16}CuPc is shown in Fig. 3. A stack of closed grains and smooth surface may be observed. Secondly, the introduction of OTS will eliminate the electron traps brought by the OH- group and at the same time the OTS hydrophobic surface also makes it less dipolar, which induces the improvement of n-type electric properties. Finally, the OTS layer in heterojunction devices is also in favour of the form of the conductivity channel (n- and p-channel), which probably gets rid of the charge traps at the interface close to the organic semiconductor. It will provide an excellent interface with low traps for charge transportation. Studies on the function of OTS in heterojunction devices are in progress. However, the first-step improvement has been achieved.

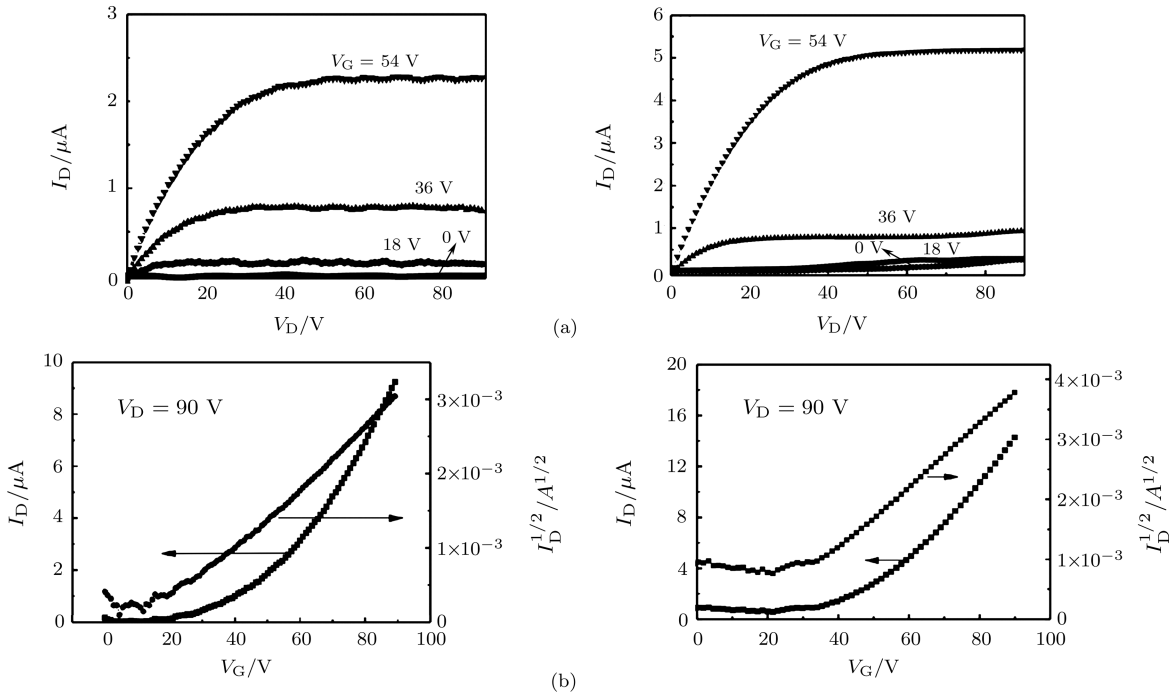


Fig. 2. (a) Output characteristics of the $F_{16}CuPc$-transistor based on the SiO_2 insulator and SiO_2/OTS insulator, respectively. (b) Transfer characteristics of the $F_{16}CuPc$-transistor based on the SiO_2 insulator and SiO_2/OTS insulator, respectively.

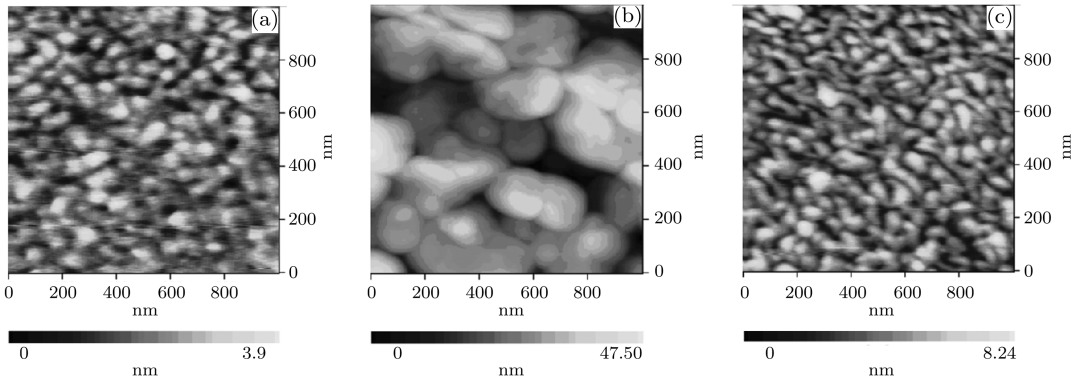


Fig. 3. AFM topographical images (1 μm × 1 μm). (a) $F_{16}CuPc$ on SiO_2/OTS, (b) pentacene on $F_{16}CuPc$, and (c) CuPc on $F_{16}CuPc$.

3.2. $F_{16}CuPc$ heterojunction TFT

3.2.1. $F_{16}CuPc$/pentacene heterojunction

An organic heterojunction exhibits unique characteristics in comparison with its inorganic counterpoint. Recently, it has been introduced to OTFTs for ambipolar charge transportation and the buffer layer of charge injection.[14,15] Here we expect to use it for high-performance n-channel devices. The $F_{16}CuPc$ is a promising n-type material with high air stability, and pentacene has the highest field-effect mobility among current p-type materials.[16,17] Therefore, this material pair was firstly selected for the expectation of high-performance. Figure 4 shows the typical output and transfer curves of $F_{16}CuPc$/pentacene heterojunction-based transistors operating in the hole-depletion and enhancement mode. The I_D increases by tuning V_G from –18 to 54 V; this implies that these devices operate normally on mode. By supplying a negative V_G of –18V, holes may be depleted, and be accumulated at a positive V_G. This phenomenon is due to the intrinsic conductivity originating from the heterojunction effect.[14] Compared with a single-layer $F_{16}CuPc$ device with an OTS modified insulator, we find that the I_D exhibits a two-fold increase from 2 μA to 4.5 μA. Although the high intrinsic con-

ductivity degrades the on/off ratio of TFT, it is still useful in p-MOS (metal–oxide–semiconductor) as a load device.[18] The device parameters were extracted from the transfer curves. The threshold voltage is –40 V, and field-effect mobility is 0.005 $cm^2/(V \cdot s)$, which is smaller than that of single-layer $F_{16}CuPc$ (0.048 $cm^2/(V \cdot s)$). This result was attributed to the mismatch of morphology that induced lots of traps at the interface of $F_{16}CuPc$/pentacene. These traps lead to poor charge injection for low device performance. In Fig. 3, AFM images of $F_{16}CuPc$ on OTS (a) and pentacene on $F_{16}CuPc$/OTS substrate (b) are presented, respectively. Due to the remarkable difference of $F_{16}CuPc$ and pentacene grains, it leads to the rms roughness of $F_{16}CuPc$ and pentacene film being 1.17 nm and 8.16 nm, respectively. This difference indicates that the distortion of grains may arise during the growth of pentacene on the substrate of $F_{16}CuPc$. This will also lower the electric characteristics of heterojunction devices. Accordingly, the match of morphology is crucial for these heterojunction devices.

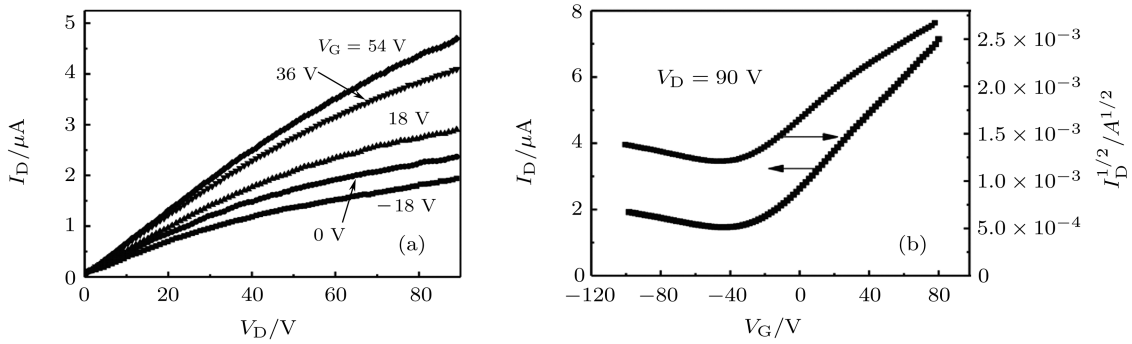


Fig. 4. Output (a) and transfer (b) characteristics of the $F_{16}CuPc$/pentacene-transistor based on the SiO_2/OTS insulator.

3.2.2. $F_{16}CuPc$/CuPc heterojunction

The electric characteristics of $F_{16}CuPc$/CuPc heterojunction transistors are shown in Fig. 5. For output curves, I_D increases with the magnitude of V_D, with transition from a linear to a saturation region, and becomes larger at higher V_G. It implies typical n-channel conductivity. Electrons in $F_{16}CuPc$ film can be gradually accumulated at the interface of the semiconductor/insulator under positive V_G and V_D. However, in the region of low, negative V_G and high V_D ($V_G = -18$ V, $V_D > 80$ V), I_D exhibits the slight super-linear increase shown in Fig. 5(a). This phenomenon indicates that a small hole current is produced which originates from the CuPc film. The electric parameters of devices are extracted from transfer curves. The field-effect mobility is 0.081 $cm^2/(V \cdot s)$, and the threshold voltage is –20 V. The I_D increased from 2.26 to 15.6 μA under the same V_G (54 V) and V_D (90 V) in comparison with single-layer $F_{16}CuPc$ devices. Moreover, the device performance has not changed for two months in air, which implies the high air stability of our device.

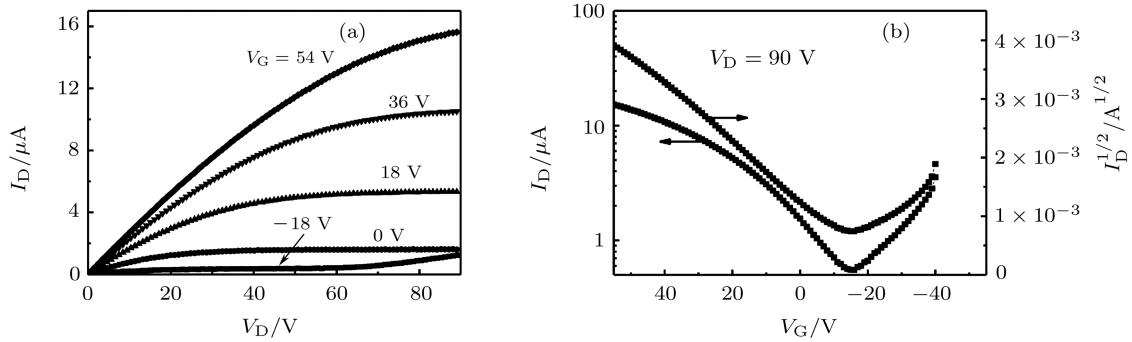


Fig. 5. Output (a) and transfer (b) characteristics of the $F_{16}CuPc$/CuPc-transistor based on the SiO_2/OTS insulator.

The dual effects of an organic heterojunction and modified insulator may be responsible for the improvement. The organic heterojunction effect has been reported for improved charge injection due to abundant free charge carriers at the interface of the heterojunction which may narrow the width of the contact potential barrier (depletion region at or near the interface of organic/metal) to the point where charge carrier tunneling occurs and considerably enhances the injection efficiency.[15] Here, the thickness of both n-type and p-type semiconductors were controlled at 10 nm to meet the accumulation width of charge.[19] In this case, lots of free charges are pulled to both sides of the heterojunction interface and form a polar layer with high conductivity. The free charge may be driven by $V_{\rm D}$ and at the same time it is also helpful for charge injection under a constant $V_{\rm G}$. In this case, the heterojunction effect presented completely, which will produce an improved charge injection. Moreover, the modified insulator induces a smooth surface and hydrophobic property, which provides an excellent surface for the growth of organic heterojunction films. Further research about OTS functions in an organic heterojunction is in progress.

However, it is noted that the organic p/n material pairs need careful selection. It also concerns morphological match and compatibility. Crystalline structure, arrangement fashion of molecules, and film thickness should be considered. For the heterojunction devices in current studies, the F_{16}CuPc/CuPc pair is better than F_{16}CuPc/pentacene. Considering the match of energy level, we find that the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of pentacene (HOMO-3.2 eV, LUMO-5.0 eV) and CuPc (HOMO-3.1 eV, LUMO-5.0 eV) are similar.[20,21] Therefore, the effect of energy level may be excluded when it is in contact with F_{16}CuPc. Another factor is the morphological effect. From the AFM image of CuPc on F_{16}CuPc, as shown in Fig. 3(c), excellent an rms roughness of 1.3 nm is observed which is comparable with that of the OTS substrate. The grain diameter of CuPc on F_{16}CuPc (36.7 nm) and on OTS substrate (54.6 nm) is close, too. So the growth process of CuPc on F_{16}CuPc is uninterrupted, and it leads to lower crystalline disfigurement. Because the CuPc is the derivate of F_{16}CuPc, it has a similar crystal structure and growth manner.[7,9] In contrast, it is very different between pentacene and CuPc grains. Pentacene often exhibits disk-like grains,[22] while CuPc exhibits rod-like grains. Therefore, crystalline distortion is inevitable, and gives rise to lots of crystal disfigurements and interspaces. This will significantly degrade the quality of the organic polycrystalline film and induce poor charge injection and transportation.

4. Conclusion

In conclusion, two high-performance n-channel organic transistors have been demonstrated based on a heterojunction and modified insulators. Compared with a single-layer device, we find that the field-effect mobility exhibits a significant improvement, and observe a 6-fold higher drain current in these devices. The highest field-effect mobility obtained from the F_{16}CuPc/CuPc-based OTFT is 0.081 $\rm cm^2/(V\cdot s)$. Both heterojunction structure and OTS play crucial roles in the improvement of device performance. Moreover, the selection of the material pair of the heterojunction must also be considered seriously due to the morphological match. Generally, a similar crystal structure and growth behavior are preferred in heterojunction fabrication. Therefore, current studies will push the development of complementary technology and the practical application of heterojunctions in organic electronics.

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