# A high mobility $C_{60}$ field-effect transistor with an ultrathin pentacene passivation layer and bathophenanthroline/metal bilayer electrodes*

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$C_{60}$ field-effect transistor (OFET) with a mobility as high as 5.17 $cm^2/V{\cdot}s$ is fabricated. In our experiment, an ultrathin pentacene passivation layer on poly-(methyl methacrylate) (PMMA) insulator and a bathophenanthroline (Bphen)/Ag bilayer electrode are prepared. The OFET shows a significant enhancement of electron mobility compared with the corresponding device with a single PMMA insultor and an Ag electrode. By analysing the $C_{60}$ film with atomic force microscopy and X-ray diffraction techniques, it is shown that the pentacene passivation layer can contribute to $C_{60}$ film growth with the large grain size and significantly improve crystallinity. Moreover, the Bphen buffer layer can reduce the electron contact barrier from Ag electrodes to $C_{60}$ film efficiently.

**Keywords:** organic field-effect transistors, $C_{60}$, Bphen, passivation layer

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In recent years, organic field-effect transistors (OFETs) have attracted much attention because of their various properties including low cost, large-area and flexibility. The OFETs can be applied in radio frequency identification tags, flexible display, and all organic circuits.[1−4] In order to realize applications such as organic complementary logic circuits, both p-type and n-type transistors are needed and should have comparable performances.[5] However, until now, much attention has been paid to the investigation of p-type (hole transport) OFETs. The high hole mobility OFETs with p-type materials, i.e. pentacene,[6] rubrene[7] serving as active layers have been developed. We note, now the p-type pentacene transistors even have been used in driven active matrix organic light-emitting diode (OLED) displays.[8] In contrast, there is a major challenge to the fabrication of high performance n-channel OFETs.

So far, many researches of n-type OFETs have focused on the synthesis of new n-type semiconductor materials which have considerable air stability and favourable electron transport ability.[9−11] As a typical n-type material, the $C_{60}$ has been studied for ten years. One problem of the $C_{60}$ transistors is that they are sensitive to the air. However, the stable $C_{60}$ OFETs, with the passivation layer used to encapsulate the device, operating in the air for more than one month was reported by Horiuchi *et al.*[12] Recently, high electron mobilities of 2.5 $cm^2/V{\cdot}s$ and 4.7 $cm^2/V{\cdot}s$ based on $C_{60}$ transistors were reported by Zhang *et al.*[13] and Ito *et al.*,[14] respectively. Thus, due to the high electric mobility and the possibility of operating in air, $C_{60}$ is still very promising to be used in commercial products.

On the other hand, the electrical characteristics of OFET are dependent not only on the properties of the semiconductor active material but also on the structure of device. There are two critical factors that

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can influence the performance of OFET. The first one is insulator surface, which means that both the roughness of dielectric surface and the surface energy of the insulator can determine the charge carrier transport in OFET.[15,16] Indeed, since most of the modulated charges lie in the channel of semiconductor near the semiconductor/insulator interface, the increased roughness leads to valleys in the channel region, which may act as carrier traps and various scatterings. The surface of insulator with suitable chemical surface energy can increase the crystallinity of the semiconductor layer and thus improve charge carrier transport.[17] Indeed, the crystallinity of the semiconductor layer is also important for increasing the performance of organic solar cells.[18] To the above situation, adopting organic polymer dielectric or surfactant such as octadecyltrichlorosilane (OTS), octadecyltrimethoxysilane (OTMS) on modifying inorganic dielectric has been widely used. The second critical factor influencing the performance of OFET is the contact between source/drain metal electrodes and the organic semiconductor. A good match between the work function of metal and the energy level of semiconductor can reduce the injection barrier, which then improves the mobility of OFET clearly. Moreover, if the metal diffuses into the organic layer to form a mixture of metal and organic, then unwanted dipole is introduced into it, which could also increase the injection barrier height and influence the performance of OFET. Hence, the introduction of a buffer layer between organic film and metal source/drain (S/D) electrodes can solve the above-mentioned problems.

In this work, bathophenanthroline (Bphen), which is widely used as electron transport layer and cathode buffer layer in organic light-emitting device[19,20] and organic solar cells,[21,22] is combined with silver (Ag) as Bphen/Ag bilayer S/D electrodes to fabricate the top contact $C_{60}$ OFET. The presence of Bphen layer at the $C_{60}$/Ag interface significantly reduces the contact barrier and may protect $C_{60}$ film from diffusing and other chemical reactions taking place between the organic layer and the metal. An ultrathin pentacene passivation layer on a PMMA insulator is adopted to improve the crystallinity of $C_{60}$ film. Then a $C_{60}$ OFET with electron mobility as high as 5.17 $cm^2/V{\cdot}s$ is fabricated.

The schematic structure of top-contact $C_{60}$ OFETs is shown in Fig. 1. PMMA was used as a gate insulator on the ITO coated glass substrate. Using chlorobenzene as a solvent, a PMMA solution was spun coated onto the substrate and baked on a hot plat at 130 °C for 2 h. The typical thickness of the PMMA insulator was approximately 400 nm. Then, a 2-nm pentacene passivation layer was deposited on the insulator at a rate of 0.2 Å/s (1 Å=0.1 nm). A typical thickness of 50-nm $C_{60}$ film was deposited on a pentacene passivation layer at a rate of 0.5 Å/s. Subsequently, 2.5-nm Bphen was deposited on $C_{60}$ film and patterned using a shadow mask with channel length $L = 125$ μm and width $W = 5$ mm. Finally, the source electrode and the drain electrode of Ag were thermally evaporated on Bphen. For comparison, the devices without pentacene passivation layer and Bphen buffer layer were fabricated in the same runs respectively. The current–voltage characteristics of OFETs were measured under nitrogen conditions with a Keithley 4200 sourcemeter at room temperature.

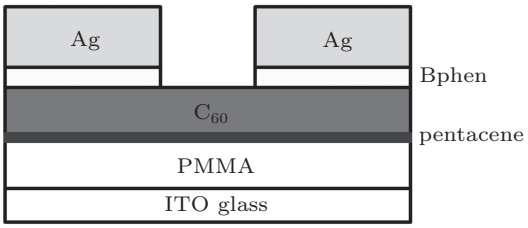



**Fig. 1.** Schematic structure of OFETs in this study.

Figure 2 shows the transfer curve $I_{DS}$–$V_{GS}$ characteristics of conventional OFETs with single $C_{60}$ layer (sample A), OFETs with only Bphen buffer layer (sample B), OFETs with only pentacene passivation layer (sample C) and OFETs with both pentacene passivation layer and Bphen buffer layer (sample D). When $V_G$ is kept at 40 V and $V_{DS}$ reaches 40 V, the $I_{DS}$ values of samples C and D are more than one order of magnitude higher than those of sample A and sample B. The result shows that $C_{60}$ OFETs with pentacene passivation layer can increase the mobility drastically. Besides, we notice that sample B and sample D, each of which has a Bphen buffer layer under S/D electrode, show not only lower voltage but also higher saturation current than those of sample A and sample C. That means that the $C_{60}$ OFETs with Bphen buffer layer can make the electrons inject from electrodes to $C_{60}$ more easily. The values of field-effect mobility ($\mu$) of OFETs are estimated in the saturation region from Fig. 2 as follows:

$$I_{DS} = \frac{W}{2L} C_i \mu (V_G - V_T)^2, \tag{1}$$

where $C_i$ is the capacitance per unit area of the insulator, $V_G$ is the gate voltage, $W$ and $L$ are the channel width and length, respectively. From Eq. (1), the highest electron field effect mobility of 5.17 $cm^2/V{\cdot}s$ in our device can be obtained in sample D, which is more than one order of magnitude higher than 0.38 $cm^2/V{\cdot}s$ in sample A. To our knowledge, there is a report showing an electron mobility of exceeding 5 $cm^2/V{\cdot}s$ obtained with the common thermal evaporation method. The on/off ratios of samples A and B are $4.4\times10^3$ and $3.1\times10^3$. Although it is reported that the on/off ratio of $C_{60}$ transistor can reach higher than $10^6$. Here we should point out that our device is normal since the off-state current is maintained at about $\sim 10^{-9}$ A level. Indeed, to improve the on/off ratio, the material should have a high purity.[13] Moreover, comparing with the samples A and B, samples C and D in which the pentacene buffer layer upon PMMA is adopted, are found to have ambipolar characteristics.

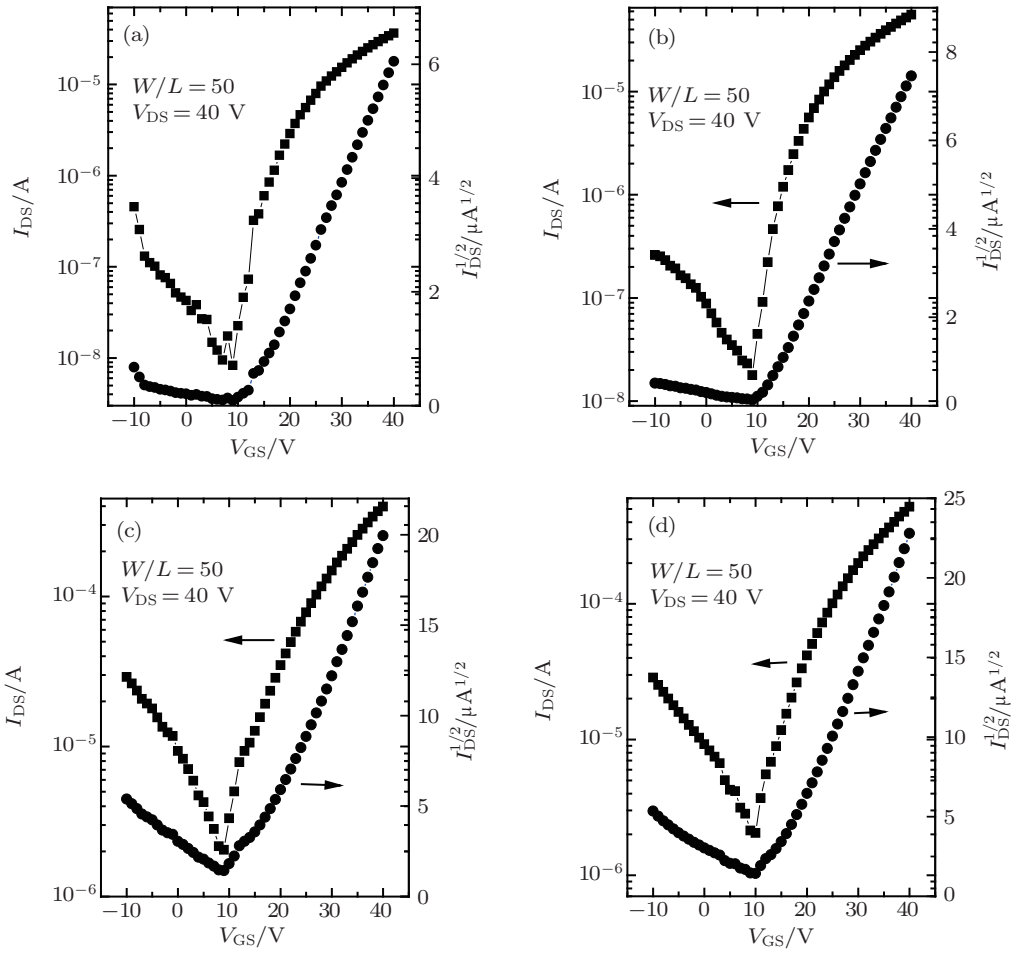



**Fig. 2.** Transfer curves of samples A, B, C and D: (a) single layer $C_{60}$ OFET; (b) OFET with 2.5-nm Bphen S/D electrodes buffer layer; (c) OFET with 2-nm pentacene passivation layer; (d) OFET with 2-nm pentacene passivation layer and 2.5-nm Bphen S/D electrodes buffer layer.

We also note that although the $I_{DS}$ values of samples C and D are more than one order of magnitude higher than those of sample A and sample B when $V_G$ is kept at 40 V and $V_{DS}$ reaches 40 V, the on/off ratios of samples C and D are smaller than those of sample A and sample B. This case can be due to the improvement of off-sate current. Indeed, when the gate voltage switches from negative to positive, the transistor operating in the p-channel accumulation mode can change to operating in the n-channel accumulation mode fast. Moreover the accumulation of electron occurs in the channel region of the $C_{60}$ thin-film caused by band bending when the contact between pentacene and $C_{60}$ takes place[23] This also may lead a bit of large current to exist when the gate voltage is very small.

Thus, the detailed characteristics of four samples are presented in Table 1.

**Table 1.** Parameters of the transistors.

| Devices | Sample A | Sample B | Sample C | Sample D |
|---|---|---|---|---|
| $\mu$/(cm$^2$/V·s) | 0.38 | 0.50 | 4.11 | 5.17 |
| $V_T$/V | 13 | 11 | 13 | 12.5 |
| On-state current/μA* | 36.63 | 55.61 | 398.01 | 519.77 |
| On/off ratio | $4.4\times10^3$ | $3.1\times10^3$ | 19.5 | 25 |

* The on-state current is the drain current when $V_G = 40$ V and $V_{DS} = 40$ V.

In order to clarify the origin of the enhancement of the OFET mobility by a pentacene passivation layer, the morphologies and the crystallinities of $C_{60}$ films with and without pentacene are measured by atomic force microscopy (AFM). Figures 3(a) and 3(b) show (AFM) images of 50-nm thick $C_{60}$ films, grown on PMMA substrates and PMMA/pentacene (2 nm) passivation layer, respectively. The larger $C_{60}$ grain size is observed in Fig. 3(b), which indicates that 2-nm pentacene passivation layer supports the crystallization of the $C_{60}$ molecules. Generally, there are many traps concentrated at the grain boundary, which can restrict the flow of charges. Here the larger grain size of $C_{60}$ film on pentacene should have less boundary traps. And thus the electrons can transport more easily.

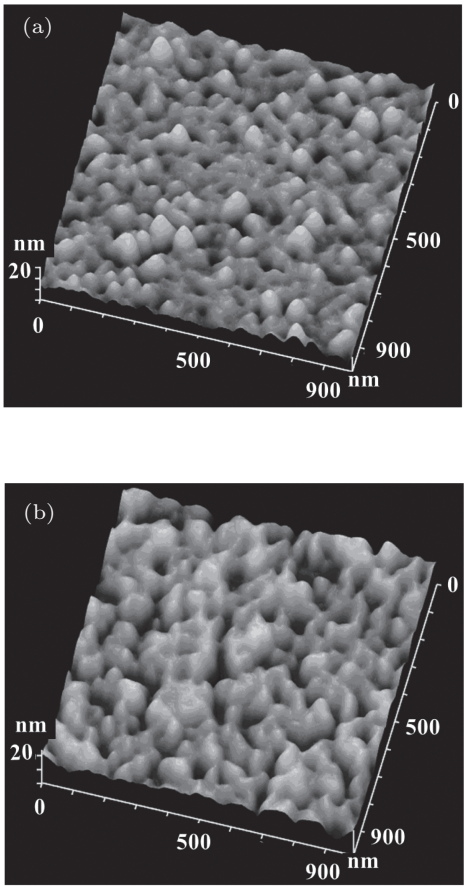



**Fig. 3.** Tapping-mode AFM images in 1 μm×1 μm of (a) 50-nm single $C_{60}$ film and (b) pentacene (2 nm)/$C_{60}$ (50 nm) on PMMA.

Figure 4 shows X-ray diffraction (XRD) patterns of the $C_{60}$ thin films simultaneously grown on PMMA substrate without and with a pentacene passivation buffer layer. The small diffraction peaks in $C_{60}$ thin films grown only on PMMA substrate show that $C_{60}$ forms a weak polycrystalline structure. The obvious diffraction peak in $C_{60}$ thin film grown on PMMA with pentacene passivation substrate demonstrates that the polycrystalline structure is much more intense. The strong intense peak of $C_{60}$ on the pentacene indicates that the polycrystalline film is grown mainly with an orientation parallel to the $c^*$-axis orient.[24] The result of XRD is in consistence with the AFM image very well. However, as the morphology and the crystallinity of pentacene film depend on the dielectric, there may have a continuous effect from the pentacene to the $C_{60}$ film when we choose the different dielectric materials.[24–26] This work is being undertaken now.

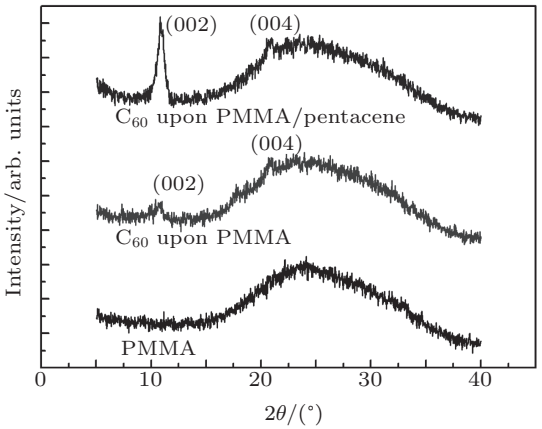



**Fig. 4.** X-ray diffraction spectra of the single $C_{60}$ (50 nm) film and pentacene (2 nm)/$C_{60}$ (50 nm) on PMMA.

Meanwhile, from Fig. 2, we observe that an inserted Bphen buffer layer can reduce the $V_T$ of devices no matter whether the pentacene passivation layer exists. In addition to the reduction of $V_T$, the mobility

of OFET with Bphen buffer layer also presents an enhancement. We should point out that since the lowest unoccupied molecular orbitals (LUMOs) of $C_{60}$ and Bphen have energies of 3.6 eV and 2.9 eV respectively, there is a large barrier formed between the LUMOs of Bphen and Ag, which seems to indicate that the electron can transport from Ag to $C_{60}$ more easily. However, in fact, the performace of OFET can be improved by inserting the Bpen buffer layer from our experiment. We suggest that the electron transport across the buffer layer occurs mainly through states induced during the deposition process of metallic cathode. This case can be found in some OFETs and organic photovoltaic cells (OPVs).[27,28] As figure 5(a) shows, a large barrier exists at the Ag/$C_{60}$ contact which can influence the performance of device seriously. With 2.5-nm thick Bphen buffer layer, work function of Ag/Bphen is reduced significantly and closer to the LUMO of $C_{60}$, which contributes to more efficient electron transport as shown in Fig. 5(b). The diffusion of the metal into the organic film can form the dipole, thereby increasing the contact energy barrier between metal and organic material.[29] Here however, due to the existence of the Bphen buffer layer protection, the metallic surface constructed prevents Ag from diffusing into the pentacene surface layer. The work function of the surface Ag is closer to that of pure Ag. Thus, by reducing the energy barrier and lessening the dipole layer, the contact resistance decreases which leads the voltage drop to decrease in the contact but to increase in the channel region. So, the hole injection efficiency and the strength of channel electric field are enhanced, the performance of device with buffer layer is improved. Moreover, besides the change of transport barrier, here the Bphen buffer layer may also provide a better contact between Ag and $C_{60}$ and protect the damages of $C_{60}$ films from thermally evaporated Ag, which could reduce the interfacial traps. We should point out that the 2.5-nm thickness of Bphen is an optimal thickness when it is applied between Ag and $C_{60}$. In our laboratory, we have found that when the thickness of Bphen increases to 8 nm, the bulk resistance of Bphen can lead to the deteriorated performance.[22]

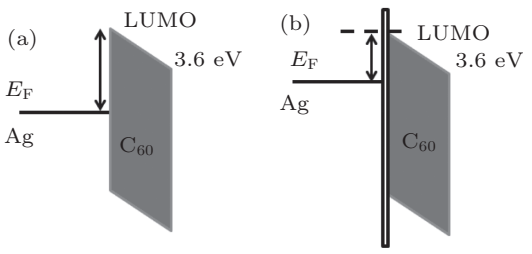



**Fig. 5.** Energy level diagrams of $C_{60}$/Ag interface: (a) without Bphen buffer layer; (b) with 2.5-nm Bphen buffer layer.

In conclusion, high mobility 5.17-$cm^2$/V·s $C_{60}$ OFET devices each with pentacene passivation layer and Bphen buffer layer are fabricated and investigated. Compared with these single $C_{60}$ layer OFET, the devices with pentacene passivation shows a drastical increase of $C_{60}$ film crystallinity, which could provide larger output current. The device with Bphen buffer layer shows an increase in electron mobility and presents a reduction in threshold voltage, which is attributed mainly to the reduction in energy barrier between Ag and $C_{60}$. Such a result may provide an effective method to improve the performance in other OFETs.

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