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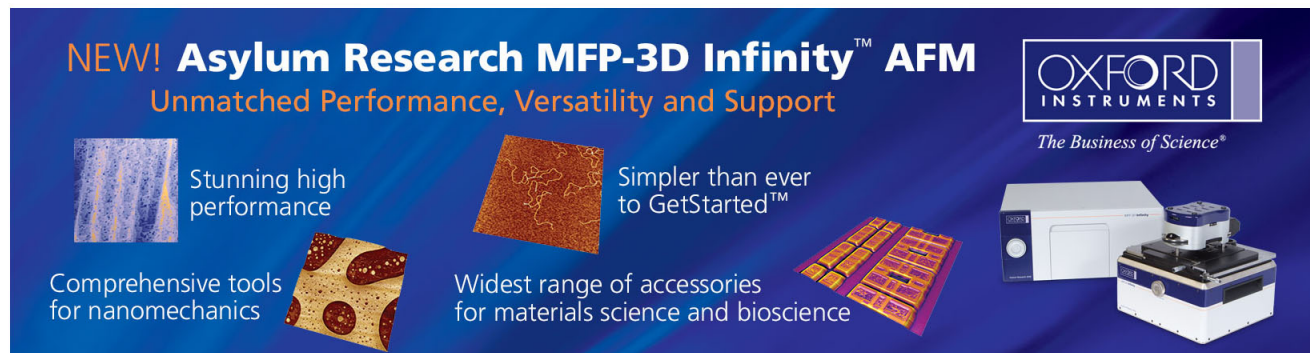Contact-metal dependent current injection in pentacene thin-film transistors
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Copper phthalocyanine buffer layer to enhance the charge injection in organic thin-film transistors

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Copper phthalocyanine (CuPC) has been used as the buffer layer for source and drain electrodes to improve the performance of organic thin-film transistors. The mobility was improved by almost onefold after the modification. By incorporating with CuPC, the contact resistance was reduced, deduced from the line-transfer method. The higher hole current observed in the hole-only diode after adding CuPC further confirms the improvement of hole-injection efficiency. It is concluded that the device improvement is attributed to the reduction of contact resistance, which resulted from the Fermi level pinning at the induced gap states at the Au/CuPC interface. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2535741]

Organic thin-film transistors (OTFTs) are of increasing interest owing to their unique properties, such as low-temperature and low-cost fabrication processes, light weight, and mechanical flexibility. The organic-based radio frequency identification tags, flexible displays, and electronic papers are under development and have great potential for commercialization.[1–4] However, further improvement of the device performance is still needed to meet the requirement of practical applications. One of the concerns is the efficiency of charge injection into the organic semiconductors. Since the surface dipoles are usually observed at the organic/metal interfaces, the contact resistance of the devices is usually significant.[5,6] Consequently, it is crucial to develop methods to improve the charge injection efficiency and to lower the contact resistances of OTFTs.

Several reports have indicated that the hole-injection efficiency can be enhanced by incorporating one inter facial layer at the source/drain and semiconductor interfaces. For example, Hajlaoui *et al.* evaporated tetracyanoquinodimethane (TCNQ), a strong electron acceptor, on oligothiophenes before the deposition of Au in a device with a top-contact configuration, improving the device mobility due to a better carrier injection.[7] Additionally, Chu *et al.* have also adopted metal oxides as the buffer layers to enhance the hole injection into pentacene.[8] With this interlayer, metals even with lower work function, such as Al, can be still used as efficient source/drain contacts. More recently, Park *et al.* introduced one layer of 4,4′,4″-tris(*N*-3-methylphenyl-*N*-phenylamino)-triphenylamine (m-MTDATA) into the device by Rigiflex lithography,[9] resulting in one order of magnitude improvement in the mobility. However, different mechanisms were proposed to explain the above examples. The doping of oligothiophenes with TCNQ results in a regime with higher conductivity and a lower injection barrier.[7] For the metal oxides, the metal/metal oxide interface should be Ohmic due to the doping induced from the evaporation

process. The reduction in the contact barrier and the prevention of metal diffusion and/or unfavorable chemical reactions are also the possible reasons.[8] On the other hand, the incorporation of m-MTDATA introduces a "ladder-step" energy level between the metal and the highest occupied molecular orbital of pentacene, which can decrease the charge-injection barrier.[9] The detailed mechanisms of the enhancement of charge injection with various interfacial layers still do not deeply examined and understood yet, partially owing to the complicated nature of the interfaces.

To further investigate the role of buffer layers, copper phthalocyanine (CuPC), which has been used extensively in the area of organic light-emitting diodes as a buffer layer,[10] was used as the interfacial layer at the source/drain contacts to reduce the contact resistance of the OTFTs. The device performance was enhanced after the modification. The improvement of the charge injection is attributed to the pinning of the Fermi level at the induced gap states, resulting in a reduction of injection barrier.

The devices were made on Si substrates, where highly doped Si and 200 nm thermal SiO$_2$ served as the gate electrode and the insulator, respectively [Fig. 1(a)]. The SiO$_2$ surface was further modified by hexamethyldisilizane to improve the device performance. Then, 60 nm of pentacene was thermally evaporated to form the semiconducting layer. CuPC with various thicknesses was deposited to be the buffer layer. Finally, gold was thermally evaporated as the source and drain electrodes through a shadow mask with a channel length (L) of 100 μm and width (W) of 2000 μm.

Figure 1(b) shows the source-drain current (I_D) versus gate voltages (V_G) of the OTFTs with Au or Au/CuPC as the source and drain electrodes. It can be seen apparently that the device with the modified electrodes (1.0 nm CuPC) has higher output current. However, while the thickness of the CuPC buffer layer exceeds 1.0 nm, the current becomes lower. The mobility (μ) of these devices were calculated at the saturation region from the following equation;
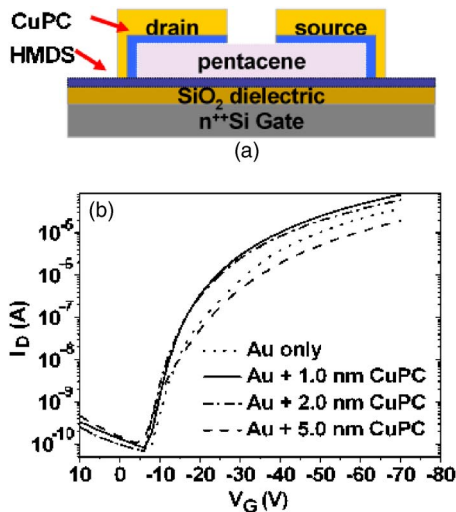
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FIG. 1. (Color online) (a) Device structure of the OTFTs in this study. (b) The transfer character of OTFTs with electrodes made of Au or Au/CuPC.
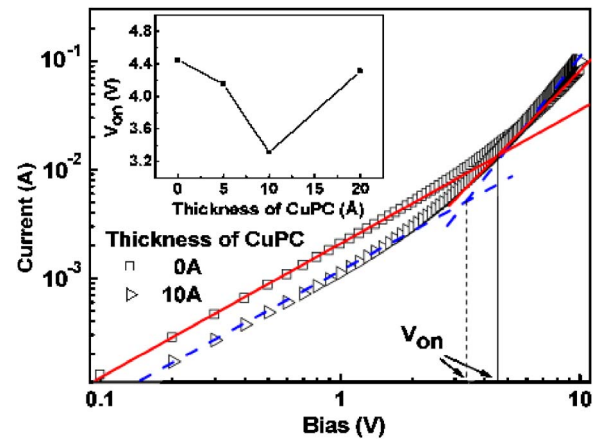

FIG. 3. (Color online) Current-voltage characteristics of the organic diodes made of pentacene with and without CuPC as the buffer layer. The device structure is ITO/PEDOT-PSS/pentacene/CuPC(x nm)/Au. The ITO electrode is defined as the cathode; the Au electrode is defined as the anode. Inset: the turn-on voltages of the devices vs the thickness of CuPC.

$$I_D = (WC_i/2L)\mu(V_G - V_T)^2, \qquad (1)$$

where C_i is the capacitance per unit area of the insulator and V_T is the threshold voltage. For the device without modification, the mobility and on-off ratio are 0.11 cm^2/V s and 5.0×10^5, respectively. On the other hand, the mobility and on-off ratio were both improved to 0.21 cm^2/V s and 1.0×10^6, respectively, after incorporating with 1.0 nm CuPC [Fig. 2(a)].

In order to clarify the role played by the interfacial layer, transfer line method was adapted to estimate the contact resistance (R_c) from the linear region of the output characteristics.[5,6] The contact resistances of the CuPC-modified devices with different thicknesses at various gate biases are shown in Fig. 2(b). For the device with 1.0 nm CuPC, the extracted contact resistance is 1.55×10^5 Ω cm, which is apparently lower than that of the device with pure Au electrodes (4.71×10^5 Ω cm) at a gate bias of -75 V. The resistances of the device with 1.0 nm CuPC are averagely lower than that of the unmodified device by 70% at different gate biases. From Fig. 2(b), it can be also observed that the contact resistance increases again if the thickness of CuPC is more than 1.0 nm. It is inferred that the increased contact resistance, while the thickness of CuPC was getting larger, is due to the intrinsically low conductivity of CuPC. Consequently, the observed mobility of the devices also decreases.

To further investigate the role of CuPC, hole-only diodes with CuPC as the buffer layer were fabricated. The device structure is indium tin oxide (ITO)/poly(3,4-

ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT-PSS)/pentacene (200 nm)/CuPC (x nm)/Au, where x is equal to 0.0, 0.5, 1.0, and 2.0. The large barrier of electron injection between PEDOT:PSS and the lowest unoccupied molecular orbital of pentacene ensures that the measured current is contributed solely from the injection of holes from the Au electrode. The current-voltage characteristics of the diodes are shown in Fig. 3. As conventional organic diodes, there are two distinct regions of operation.[11] Below the "turn-on" voltage (V_{on}), the current (I) increased linearly with voltage. Above the V_{on}, the current was space-charge limited, following $I \sim V^2$. V_{on} is defined as the intersection of the fitting curves of two regions, implying the voltage at which the holes start to inject. Apparently, the V_{on} decreased after modifying with 1.0 nm CuPC. Furthermore, V_{on} increased again when the thickness of CuPC is larger than 1.0 nm (the inset of Fig. 3). This observation is very similar to that of OTFTs, which confirms that the hole injection from Au to pentacene can be promoted after incorporating a thin layer of CuPC. The consistence of the optimized CuPC thicknesses (1.0 nm) suggests that the improvement is quite general for Au/pentacene interfaces.

The interface between gold and pentacene has been studied by ultraviolet photoemission spectroscopy (UPS).[12,13] For the interface formed by depositing of Au on pentacene, the results indicate the presence of an interface dipole at the interface [Fig. 4(a)], which leads to a relative large hole-injection barrier ($\sim$1.0 eV) from Au to pentacene. On the other hand, it has also been reported that a charge transfer
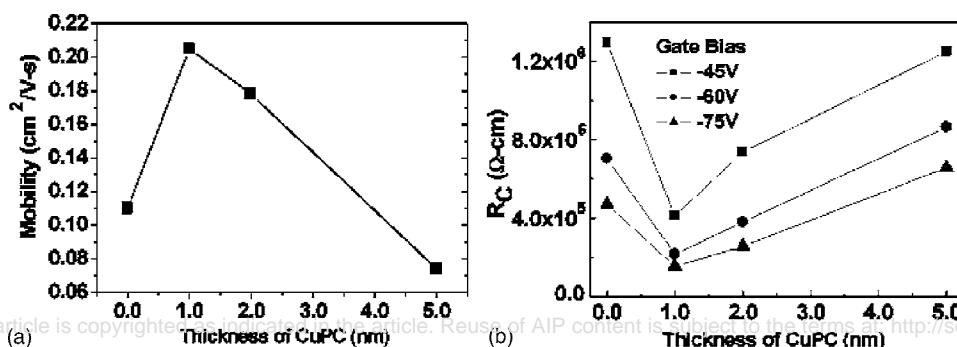

FIG. 2. (a) Mobility of the OTFTs with different thicknesses of CuPC. The mobility increases sharply as 1.0 nm CuPC is deposited but decreases as the thickness of CuPC is larger than 1.0 nm. (b) The contact resistance of the OTFTs with different thicknesses of CuPC. The contact resistances were extracted by transfer line method.
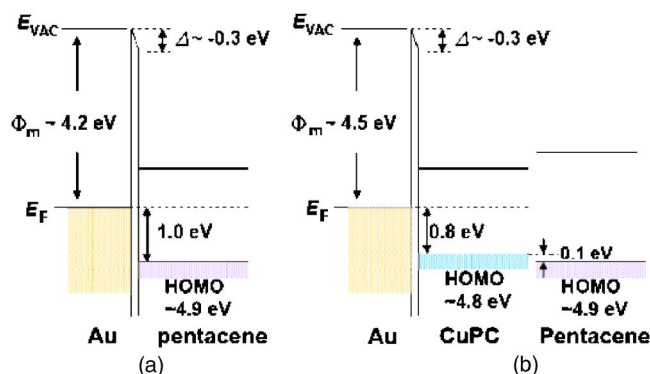
FIG. 4. (Color online) Energy level diagram of (a) Au/pentacene and (b) Au/CuPC/pentacene. The vacuum level shift is resulted from the formation of dipole layer in the interface.

from Au particles to CuPC occurs when a thin layer of Au was deposited on CuPC thin films.[14,15] By using UPS and inverse photoemission spectroscopy, Watkins *et al.* not only found a gap state, which is attributed to the charge transfer, but also observed the Fermi level pinning at the evolving state.[15] Consequently, the pinning of the Fermi level at the unoccupied gap states has also observed directly. As a result, the energy levels at the Au/CuPC interface are depicted in Fig. 4(b), where the Fermi level is pinned at the midgap of CuPC. Observably, the injection barrier is smaller between Au and CuPC than that between Au and pentacene. If we assume that no interface dipole is formed between CuPC and pentacene, owing to their similar electron-donating natures,[16] the injection barrier is indeed smaller after incorporating one thin layer of CuPC. On the other hand, CuPc itself is intrinsically low-mobility materials. Once the thickness of CuPC increases, the bulk resistance of CuPC will contribute to the device and will eventually make the device characterizes degraded.

In conclusion, it has been shown that the device performance can be improved by modifying the source/drain electrodes with 1.0 nm CuPC. The device performances such as mobility and on-off ratio were improved. The contact resistance was decreased after the modification, deduced from the line-transfer method. In addition, the lower turn-on voltage of the hole-only diode incorporating with CuPC also confirms the improvement of hole-injection efficiency. Finally, from the previously reported UPS results, it is inferred that the lower injection barrier resulted from the induced gap states at the Au/CuPC interfaces.

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