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High-Performance Low-Cost Organic Field-Effect Transistors with Chemically Modified Bottom Electrodes

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Organic field-effect transistors (OFETs) have been widely studied due to their potential application in integrated circuits for large-area, flexible, and ultralow-cost electronics.[1] Most research works in this area in the past decade have primarily focused on improving the intrinsic electrical properties of the organic semiconductors and on developing the device fabrication techniques.[2,3] Electrode materials have not attracted sufficient interest, despite their critical roles in OFETs.[4] The electrodes have to be energetically compatible with the organic semiconductors to form an ohmic contact for efficient charge injection, while they must be chemically stable to the semiconductors and gate dielectrics to prevent adverse chemical interactions at the interfaces. Most reports of the high-performance OFETs were with the gold source−drain (S−D) electrodes due to the high conductivity, outstanding operational stability, and ability to form excellent contact with most p-type organic semiconductors. Unfortunately, the high cost of gold has overshadowed its applications in low-cost electronics. Using low-cost metal for the S−D electrodes is an effective approach to dramatically reduce the cost. However, OFETs with low-cost metal electrodes such as silver (Ag) and copper (Cu) have poor properties because both Ag and Cu are energetically incompatible with most of the organic semiconductors. Recently, carboxylic acid-modified silver nanoparticles have been successfully used as the S−D electrodes to fabricate high-mobility OFETs.[4e] The results indicate that chemical modification of the low-cost electrodes could be an efficient way toward low-cost high-performance OFETs.

OFETs are fabricated in either the top- or bottom-contact S−D geometry. It has been demonstrated that the top-contact configuration, the most widely used geometry, provides a better performance compared with that of the bottom one. However, the top-contact geometry exhibits a significant obstacle to manufacturability application, i.e., incompatibility with photolithographic processes.[4a,b] Thereby, the bottom-contact configuration is a feasible geometry in practical application. Unfortunately, the devices with bottom contact suffer from lower performance due to worse metal/organic contact.

In this communication, we report a simple way to resolve the energetic mismatch of Ag or Cu S−D electrodes with the organic semiconductors and the worse interface contact in the bottom-contact configuration by modifying their interface with charge-transfer complexes. The low-cost pentacene transistors with Ag-TCNQ (TCNQ = 7,7,8,8-tetracyanoquinodimethane)-modified Ag bottom-contact electrodes exhibit outstanding properties, which are comparable with those of the Au top-contact device. It can thus offer a general solution to fabrication of the high-performance low-cost bottom-contact transistors using the Ag or Cu as S−D electrodes.

It is well-known that TCNQ can easily react with Cu or Ag to form a charge-transfer compound Cu-TCNQ or Ag-TCNQ, which exhibits unique electrical properties.[5] We modified Ag or Cu S−D electrodes, which are deposited on n-doped silicon wafers with a SiO_2 dielectric layer, with TCNQ (Figure 1). Prior to fabrication of the S−D electrodes, the SiO_2 surface was treated by octadecyltrichlorosilane (OTS) to obtain a hydrophobic surface. After modification of the electrodes, formation of the hydrophobic surface can greatly reduce any remaining TCNQ on the SiO_2 surface and thus results in a small leakage current for the fabricated OFETs. Finally, the organic semiconductors were thermally evaporated. Figure 2 shows scanning electron microscopy (SEM) images of the Ag electrode and pentacene thin films. When the TCNQ solution in acetonitrile was dropped onto the surface of the Ag electrodes, Ag-TCNQ was grown and was in good mechanical contact with the Ag electrodes. Note that the dense Ag-TCNQs couple directly to the edges of the Ag electrodes after the modification. The pentacene films deposited on the Ag-TCNQs have a strip crystal structure with a length of 400−800 nm, whereas ones on the SiO_2 and Ag surfaces exhibit smaller crystal grains with average diameters of 100−200 nm (Figure S3). Similar phenomena were observed for the TCNQ-modified Cu electrode. These results indicate that pentacene possesses a better contact with metal-TCNQ compared with the bare metal electrode. To obtain the contact resistant between the S−D electrodes and the semiconductor layer, channel length scaling analysis was performed (Figure S6). The contact resistance was reduced obviously when the Cu or Ag electrode was modified. Therefore, modification of the organic/electrode interfaces by self-assembling metal-TCNQ played an important role in improving the contact between the electrode and semiconductor layer. The excellent bottom contact could be attributed to reduction of the contact resistance. Meanwhile, the metal-TCNQ coupled between the organic semiconductor and the electrode would prevent metal diffusion into the organic layer and/or unfavorable chemical reaction.

OFET performances depend largely on the carrier injection barrier between the S−D electrodes and the organic semiconductor. It has been demonstrated that, when the metal Cu was covered with Cu-TCNQ, the work function increased from 4.6 to 5.2 eV.[6] Therefore, the formation of a metal-TCNQ charge-transfer layer could lead to an obvious increase of the electrode's work function, which can decrease the carrier injection barrier.

A series of bottom-contact pentacene OFETs with modified Ag (or Cu) S−D electrodes were fabricated. For comparison, devices with the bare Ag (or Cu) bottom electrodes as well as the Au top

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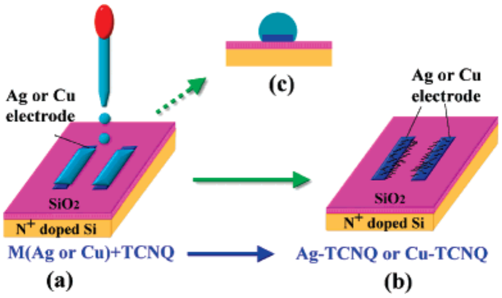

Figure 1. Schematic illustration for modification of the Ag (or Cu) electrodes by Ag-TCNQ (or Cu-TCNQ). (a) Dropping TCNQ solution in acetonitrile onto the OTS-modified SiO_2 with the bottom patterned Ag or Cu source-drain electrodes. (b) The modified source−drain electrode. (c) The TCNQ solution is aggregated on the Ag or Cu surfaces due to hydrophobicity of the OTS-modified SiO_2 surfaces.

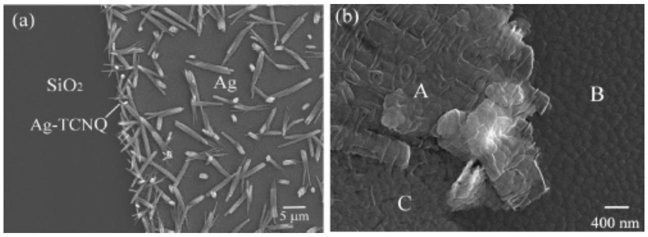

Figure 2. SEM images of (a) the Ag-TCNQ modified Ag electrodes and (b) pentacene deposited on the surface of (A) Ag-TCNQ, (B) SiO_2, and (C) Ag.

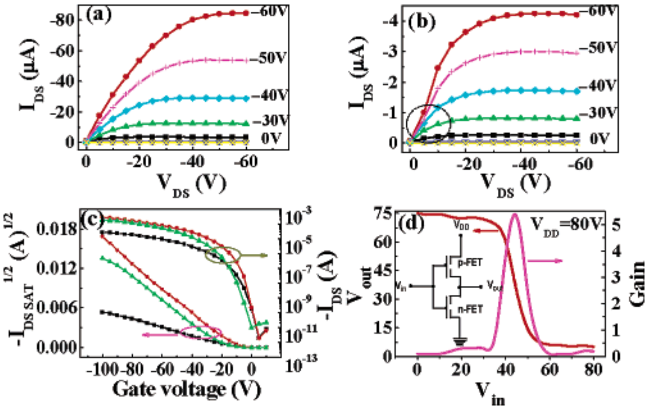

Figure 3. Output characteristics of the pentacene bottom-contact OFETs: (a) with the Ag-TCNQ modified Ag S−D electrodes; (b) with the bare Ag electrodes. (c) Transfer characteristics of the transistor based on pentacene with different electrodes, (■) the Ag bottom-contact electrode, (●) Ag-TCNQ/Ag bottom-contact electrode, and (▲) Au top-contact electrode. (d) Transfer characteristics and measured gain of a complementary inverter formed by using F_{16}CuPc n-channel and pentacene p-channel OFETs with the Ag-TCNQ modified Ag S−D electrodes. (Inset) Layout of the inverter.

electrodes were also prepared. Figure 3a shows output characteristics of the pentacene bottom-contact OFETs with the Ag-TCNQ modified Ag S−D electrodes. The linear current−voltage relationship at source−drain voltage < gate voltage indicates that the OFETs with the Ag-TCNQ-modified electrodes have ideal ohmic contact characteristics. On the other hand, contact resistance arising from energetic mismatch was directly observed in the output curves of the OFETs with the bare Ag S−D electrodes: a characteristic S-shaped curve in the linear regimes (Figure 3b). The devices with the Ag-TCNQ-modified electrodes gave a mobility of 0.18 $cm^2\ V^{-1}\ s^{-1}$ and on/off ration of 10^6, which are similar to those of the devices with the Au top-contact electrodes (0.15 $cm^2\ V^{-1}\ s^{-1}$ and 10^6). To the best of our knowledge, the mobility of 0.18 $cm^2\ V^{-1}\ s^{-1}$ is the highest value reported for the organic bottom-contact OFETs with the Ag S−D electrodes. The Cu-TCNQ-modified devices also show outstanding performances in comparison with the devices with the Cu electrodes (Table S1). The analogous phenomena were observed in the bottom-contact devices based on both copper phthalocyanine (CuPc) and hexadecafluoro-copper phthalocyanine (F_{16}CuPc). Moreover, the devices with modified S−D electrodes exhibit comparable stability with devices using the Au electrodes (Figure S8). The ability to form high-performance n- and p-channel transistors with the Ag-TCNQ-modified bottom electrodes enables complementary inverter circuits. To illustrate this capability, we built arrays of inverters with the F_{16}CuPc and the pentacene FETs (Figure 3d). These circuits exhibit gains greater than 5.

In conclusion, we report on the excellent electrical properties of low-cost organic transistors and inverters that use the M-TCNQ (M = Ag or Cu)-modified Ag or Cu S−D electrodes in bottom-contact configurations. The contact resistance and energetic mismatch typically observed with the low-cost bare electrodes in the petacene bottom-contact OFETs can be properly eliminated.

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Supporting Information Available: Device/film fabrication and characteristics; contact resistance measurement. This material is available free of charge via the Internet at http://pubs.acs.org.

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