High-performance organic thin-film transistors with metal oxide/metal bilayer electrode

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We demonstrate bilayer source-drain (S-D) electrodes for organic thin film transistors (OTFT). The bilayer consists of a transition metal oxide (MoO$_3$, WO$_3$, or V$_2$O$_5$) layer and a metal layer. The metal oxide layer, directly contacting the organic semiconducting layer, serves as the charge-injection layer. The overcoated metal layer is responsible for the conduction of charge carriers. We found that the metal oxide layer coupled between pentacene and metal layers played an important role in improving the field-effect transistor characteristics of OTFTs. Devices with the bilayer S-D electrodes showed enhanced hole-injection compared to those with only metal electrode. High field-effect mobility of 0.4 cm$^2$/V s and on/off current ratios of 10$^4$ were obtained in the pentacene based TFTs using the bilayer S-D electrodes at a gate bias of $-40$ V. The improvement is attributed to the reduction in the contact barrier and the prevention of metal diffusion into the organic layer and/or unfavorable chemical reaction between the organic layer and the metal electrode. © 2005 American Institute of Physics. [DOI: 10.1063/1.2126140]

Substantial progress has been made in developing high-performance organic semiconductors in the past decade. Organic semiconducting materials have been used to fabricate transistors, with electronic properties similar to hydrogenated amorphous silicon ($a$-Si:H), a material often used for flat panel displays. For example, field-effect mobilities greater than 1 cm$^2$/V s with large on/off current ratio have been reported for pentacene thin film transistors (TFTs). Such comparable electronic characteristics, together with the advantage of low temperature and low cost fabrication on various conformable substrates, make organic thin film transistors (OTFTs) attractive candidates for use in commercial products. Although a large number of studies have focused on improving the intrinsic electrical properties of the organic semiconductors and towards the development of device fabrication techniques, the contact between the electrodes and the active layer, which is critical to OTFT device performance, has not received much attention.

The range of electronic properties of the transition metal oxides offers a unique opportunity to control the work function, and hence, the charge-injection properties. Therefore, modification of the organic/electrode interface by inserting a transition metal oxide has received considerable attention in regards to organic electroluminescent devices. Similarly, the source-drain (S-D) contacts in the organic TFTs have significant influence on device operation, through their contribution to the contact resistance arising from mismatch of the work functions, and/or interaction between the metal electrodes and the organic semiconductor. Inserting a transition metal oxide, such as MoO$_3$, between the S-D contact and organic active layer can greatly reduce the contact resistance for the organic TFTs.

Aluminum (Al) is a well-known contact material in integrated circuits and exhibits good corrosion resistance. However, its low-work function precludes the application of Al to high performance OTFT for $P$-type semiconductors. On the other hand, high performance OTFTs can be achieved by inserting a transition metal oxide layer between Al S-D electrodes and organic semiconductors. In this letter, we show that the performance of OTFTs with the MoO$_3$/Al S-D electrodes greatly improved over those ones with Al, or even gold (Au), as the S-D electrodes. The presence of MoO$_3$ layer at the organic/Al interface significantly reduces the contact barrier and provides protection from diffusion and other chemical reactions between the organic layer and the metal.

The schematic structure of top-contact pentacene TFT and the energy level diagram are shown in Figs. 1(a) and 1(b). The devices were made using heavily-doped $P$-type silicon wafers with a 300-nm-thick SiO$_2$, which functioned as the gate electrode and the gate insulator, respectively. Prior to pentacene active layer deposition, the SiO$_2$ surface was cleaned by UV/O$_3$ cleaner and chemically-modified using silane coupling agent octadecyltrichlorosilane. Following the gate insulator treatment, a 40-nm-thick layer of pentacene (Sigma-Aldrich, ~98% purity) was thermally evaporated at the rate of 0.5 Å/s from a molybdenum boat. Finally, MoO$_3$ (Sigma-Aldrich, 99.99% purity) and Al were thermally evaporated onto the pentacene film through a shadow mask to form the S-D electrodes with a channel length of 100 μm and width of 5 mm. The thicknesses of MoO$_3$ and Al films were 20 and 50 nm, respectively. In addition, Au and Al were investigated as alternatives to the MoO$_3$/Al as S-D contacts. All the materials were used without any further purification. All thermal evaporation were done under a pressure of less than 6 × 10$^{-6}$ Torr while monitoring the film thickness with a quartz oscillator. Electrical measurements were performed in a vacuum of 10$^{-5}$ Torr at the room temperature using an HP 4155B semiconductor parameter analyzer.

Figure 2(a) shows the source-drain current ($I_{DS}$) versus source-drain voltage ($V_{DS}$) of the OTFT with Al/MoO$_3$ as the S-D electrodes at different gate voltages ($V_G$). The device showed typical $P$-channel characteristics. As can be noted,
the output characteristics displayed very good, clear saturation currents which behaved quadratically as a function of the gate bias. The corresponding plots of $-I_{DS}$ and $(I_{DS})^{1/2}$ versus $V_G$ for the device are shown in Fig. 2(b). Strong field-effect modulation of the channel conductance was observed, with on/off current ratios ($I_{on}/I_{off}$) as high as $10^4$ (measured between gate voltage, $V_G = -40$–$10$). The field-effect mobility ($\mu$) was calculated at the saturation regions from the following equation:

$$I_{DS} = (WC/2L)\mu(V_G - V_T)^2,$$

where $C_i$ is the capacitance per unit area of the insulator, and $V_T$ is the threshold voltage. The field-effect mobility and the threshold voltage of the OTFT were 0.40 cm$^2$/V s and $-10.43$ V, respectively. On the other hand, Figs. 3(a) and 3(b) show $I_{DS}$ versus $V_{DS}$ curves for the OTFTs with Au and Al as the S-D electrodes, respectively. Both these devices showed typical P-channel characteristics as well. The transfer characteristics for different materials for the S-D electrodes are shown in Figs. 4(a) and 4(b). The device with Au S-D electrode had similar $I_{on}/I_{off}$ compared to the device with MoO$_3$/Al S-D electrode, while $I_{on}/I_{off}$ for the Al electrode was $10^2$. In addition, the decreased slope of the transfer characteristics corresponded to a twofold decrease in the field-effect mobility to $\mu_{th} = 0.18$ cm$^2$/V s for the Au contacts. For the case of Al, the saturation current of the channel further reduced, and field-effect mobility of $2.8 \times 10^{-3}$ cm$^2$/V s was calculated. These results demonstrate that the introduction of the metal oxide in our OTFTs played an important role in decreasing the contact resistance. Other metal oxides were combined with Al for the S-D electrodes and the electrical characteristics of the OTFTs with different S-D electrodes in this study are summarized in Table I.

In order to understand the performance improvement in the devices with MoO$_3$/Al as electrodes, we must consider the electronic properties of the transition metal oxide. The energy level diagrams for pentacene, MoO$_3$, Au, and Al are illustrated in Fig. 1(b). MoO$_3$ is a wide gap semiconductor with band gap of $3$–$3.1$ eV, and an electron affinity of around $2.2$ eV,$^{11,12}$ which implies the valance band position at around $5.3$ eV. The highest occupied molecular orbital (HOMO) of pentacene lies at $5.0$ eV$^{13}$ and is aligned with the valence band of MoO$_3$, resulting in no barrier for injection of holes into the pentacene layer. It has been suggested that the excess constituent can act as doping centers.

FIG. 1. (a) Structure of the organic thin film transistor; (b) energy level diagrams of pentacene, MoO$_3$ and the metals (Al, Au).

FIG. 2. (a) Source-drain current-voltage characteristics of the OTFT with MoO$_3$/Al electrodes. (b) The transfer characteristics of the OTFT with MoO$_3$/Al electrodes at a constant drain voltage of $-40$ V.

FIG. 3. Source-drain current-voltage characteristics of the OTFT where the source-drain electrodes are: (a) Au and (b) Al.
MoO₃ layer interface provides protection against metal diffusion, and this dopant controls the electrical properties of the film. Since MoO₃ layer was deposited by evaporation, MoO₃ yields a film containing species from MoO to MoO₃. To further demonstrate this, devices were fabricated using MoO₃ powder as the source-drain contacts. The width of the depletion region between metal and MoO₃ junction decreases as the doping concentration in the MoO₃ film increases; as a result, the probability of tunneling through the barrier increases. Therefore, an Ohmic contact is likely to be achieved at the metal and MoO₃ interface. To optimize the interfacial interaction, devices were fabricated using different metal electrodes (Au, Ag, and Al) as the source-drain contacts. The transfer characteristics of OTFTs using MoO₃ covered with different metals as the source-drain contacts are shown in Figure 5. The On-off ratio of OTFTs using MoO₃ covered with different metals as the source-drain contacts is given in Table I.

TABLE I. Electrical parameters of the OTFTs in this study.

<table>
<thead>
<tr>
<th>Drain-source electrodes</th>
<th>Mobility (cm²/V s)</th>
<th>Threshold voltage (V)</th>
<th>On-off ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>2.8 × 10⁻³</td>
<td>−16.2</td>
<td>2.3 × 10⁴</td>
</tr>
<tr>
<td>Au</td>
<td>0.182</td>
<td>−8.75</td>
<td>2.8 × 10⁴</td>
</tr>
<tr>
<td>MoO₃/Al</td>
<td>0.4</td>
<td>−12.1</td>
<td>3.8 × 10⁴</td>
</tr>
<tr>
<td>WO₃/Al</td>
<td>0.253</td>
<td>−12.88</td>
<td>4.1 × 10⁴</td>
</tr>
<tr>
<td>V₂O₅/Al</td>
<td>0.226</td>
<td>−10.43</td>
<td>1.8 × 10⁴</td>
</tr>
</tbody>
</table>

In conclusion, the OTFTs with MoO₃ as a hole injection layer show improved performance compared to metal-only electrodes. The interface dipole immediately forms increasing the barrier height between metal and pentacene. The modified MoO₃ layer interface provides protection against metal diffusion into the organic layer and an unfavorable chemical reaction between organic and metal electrodes. The modifi-