Improvement of Crystallinity for F\textsubscript{16}CuPc Thin Film by DH-α6T Quasi-monolayer

Rongbin Ye, Yuya Sasaki

Abstract—In this paper, we have reported on improvement of crystallinity for fluorinated copper phthalocyanine (F\textsubscript{16}CuPc) thin film by an α,α’-dihexylsextihiophene (DH-α6T) quasi-monolayer. By the detailed XRD and SEM analysis, highly ordering α-F\textsubscript{16}CuPc thin films could be deposited on SiO\textsubscript{2}/Si substrates modified by a DH-α6T quasi-monolayer. The F\textsubscript{16}CuPc/DH-α6T TFT worked in hole-enhancement and electron-depletion modes with their hole and electron mobilities of 4.10 \times 10^{-2} \text{cm}^2/\text{V}s and 2.19 \times 10^{-2} \text{cm}^2/\text{V}s, respectively. The bilayer device shows high electron mobility that is about 6 times greater than that of the single layer device, which originated from highly ordering and increasing of grain size of F\textsubscript{16}CuPc thin films deposited on a DH-α6T quasi-monolayer.

Index Terms—Organic semiconductors; organic thin film transistors; crystallinity; field-effect mobility.

I. INTRODUCTION

Metal phthalocyanines (MPCs) are organic dye materials, used in printing inks, as colorants for plastics and fibers, and their semiconductor properties are exploited for applications such as thin film transistors (TFTs), light emitting diodes, solar cells and gas sensors. [1-15] F\textsubscript{16}CuPc is one of a few air-stable n-type organic semiconductors with a low electron field-effect mobility. [3] In the previous studies, the performance of TiOPc and F\textsubscript{16}CuPc TFTs were improved utilizing DH-α6T submonolayer or employing an organic heterojunction buffer layer to decrease the contact resistance of conductive channel, respectively. [16, 17] On the other hand, organic pn heterojunction TFTs based on F\textsubscript{16}CuPc exhibit typical ambipolar conduction. In this study, we report on improvement of crystallinity for F\textsubscript{16}CuPc thin film by DH-α6T quasi-monolayer and simultaneously formation of organic ambipolar pn heterojunction TFT.

II. EXPERIMENTAL DETAILS

Figure 1 shows the chemical structures of DH-α6T and F\textsubscript{16}CuPc, and the schematic structure of organic TFT. Heavily n-doped Si substrate acts as the gate electrode with a 300 nm thermally grown SiO\textsubscript{2} layer (C\textsubscript{v}~10 \text{nF/cm}^2) as the gate dielectric. The sample of DH-α6T and F\textsubscript{16}CuPc were purchased from Sigma Aldrich. DH-α6T thin film of approximately 5 nm thickness (first layer) and F\textsubscript{16}CuPc thin film of approximately 20 nm thickness (second layer) were vacuum deposited from two deposition sources. During deposition, substrate temperature was set at 120 °C under a base pressure of less than 1\times10^{-3} \text{Pa}. The substrate temperature was controlled by a digital programming regulator (CHINO KP1000). Film thicknesses and growth rate were monitored by a thick-ness and growth rate monitor (ULVAC CRTM-6000). Finally, Au source and drain electrodes of 20 nm were vacuum deposited through a shadow mask with a channel with a channel width of 1 mm and length of 50 \mu.m. The characteristics of OTFTs were measured using a two-channel voltage current source/monitor system (Advantest R6245) under ambient laboratory air condition.

The XRD analysis was performed on a diffractometer (Rint 2200V, RIGAKU Co., Ltd.) with graphite monochromatized CuKα radiation (λ=1.54 Å), operating in the Θ-2Θ mode. The morphology of the films were examined using scanning electron microscope (SEM) (JSM-7001F, JEOL) and AFM (Nanocute, Seiko Instruments Co., Ltd.), the cantilevers were used in the tapping mode with a length of 90 \mu.m and a force constant of 0.12 N/m.

Figure 1 Chemical structures of F\textsubscript{16}CuPc and DH-α6T, and schematic structure of organic ambipolar pn heterojunction TFT

III. RESULTS AND DISCUSSION

In Fig. 2(a), the typical XRD patterns of DH-α6T thin film of 5 nm with d\textsubscript{200} spacing of 3.34 nm (2Θ = 2.64°) was observed, and DH-α6T molecules are standing up with respect to substrate surface. Figure 2(b) shows XRD patterns of F\textsubscript{16}CuPc thin films of 20 nm deposited on SiO\textsubscript{2}/Si substrate at 120 °C. Only a-form F\textsubscript{16}CuPc with the 200 plane spacing d\textsubscript{200} = 1.43 nm is observed [3]. The two XRD peaks correspond to (200) and (400) reflections. The XRD pattern of F\textsubscript{16}CuPc films deposited on DH-α6T quasi-monolayer modified SiO\textsubscript{2}/Si substrates at 120 °C was displayed in Fig. 2(c). The same two XRD peaks correspond to (200) and (400) reflections are observed, and the value of d\textsubscript{200} (1.41 nm) is slightly smaller than that of DH-α6T thin films deposited on SiO\textsubscript{2}/Si substrates. [18] Moreover, the appearance of the eighth-order diffraction peak at 18.77° (d\textsubscript{208} = 0.472 nm) further enhanced the high order of the vacuum deposited films.

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Figure 2 XRD patterns of (a) DH-α6T thin film of 5 nm, (b) an F16CuPc single layer of 20 nm and (c) a 20 nm/5 nm of F16CuPc/DH-α6T bilayer deposited on SiO2/Si substrates at 120 °C.

Figure 3 AFM images of (a) a DH-α6T of 5 nm with cross-sectional profile data corresponding to the black line, the SEM images of (b) the F16CuPc single layer of 20 nm deposited on SiO2/Si substrate and the F16CuPc/DH-α6T bilayer (All thin films deposited on SiO2/Si substrates at 120 °C).

Figure 4 Output characteristics of F16CuPc/DH-α6T TFT working in (a) hole-enhancement and (b) electron-depletion modes.

The growth behavior of the DH-α6T thin film has been studied systematically. A highly-ordered large-sized and smooth DH-α6T quasi-monolayer can supply a high quality substrate for the growth of phthalocyanine molecules. F16CuPc molecules can be oriented after the employment of the DH-α6T buffer layer. The image of the F16CuPc/DH-α6T film shows a strip grain pattern in Fig. 3(c).

Figure 4 shows output characteristics of F16CuPc/DH-α6T TFT working in hole-enhancement and electron-depletion modes. A bulk current in the device at \( V_G = 0 \) V could be observed, which originates from the charge carriers at the interface of F16CuPc/DH-α6T. [19] \( \mu \) and \( V_T \) were extracted in the linear region as followed:

\[
I_D = \frac{W}{L} C_\parallel (V_G - V_T) V_D \quad (V_G \gg V_D),
\]

where \( W \), \( L \), and \( C_\parallel \) are the channel width, channel length, and gate dielectric capacitance per unit area, respectively. Hole and electron mobilities of 4.10 x 10^-2 cm²/Vs and 1.95 x 10^-2 cm²/Vs, respectively, were derived in the linear regime and listed in Table I. The bilayer device shows high electron mobility that is about 6 times greater than that of the single layer device, which originated from highly ordering and increasing of grain size of F16CuPc thin films deposited on a DH-α6T quasi-monolayer. Although enhanced n-type characteristics could not be obtained, these ambipolar mobilities are 2~10 times greater than those of the ambipolar device based on DH-α6T/F16CuPc thin films. [20] Furthermore, thermal annealing could depress the bulk current, which is harmful to device performance such as current on/off ratio. [16, 20] Theremore, performance of the F16CuPc/DH-α6T bilayer device could be expected to be improved by thermal annealing process.
Table 1  Summary of mobilities for the DH-α6T quasi-mono layer, the F16CuPc single layer and the F16CuPc/DH-α6T bilayer devices.

<table>
<thead>
<tr>
<th>Active layer</th>
<th>μp (cm²/Vs)</th>
<th>μn (cm²/Vs)</th>
</tr>
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<tbody>
<tr>
<td>DH-α6T quasi-mono layer</td>
<td>2.99 x 10⁻²</td>
<td>-</td>
</tr>
<tr>
<td>F16Pc single layer</td>
<td>-</td>
<td>3.56 x 10⁻³</td>
</tr>
<tr>
<td>DH-α6T/TiOPc bilayer</td>
<td>4.10 x 10⁻²</td>
<td>1.95 x 10⁻²</td>
</tr>
</tbody>
</table>

IV. CONCLUSION

In this study, we have reported on improvement of crystallinity for F16CuPc thin film by a DH-α6T quasi-mono layer. By the detailed XRD and SEM analysis, highly ordering α- F16CuPc thin films could be deposited on SiO₂/Si substrates modified by a DH-α6T quasi-mono layer. The F16CuPc/DH-α6T TFT worked in hole-enhancement and electron-depletion modes with their hole and electron mobilities of 4.10 x 10⁻² cm²/Vs and 2.19 x 10⁻² cm²/Vs, respectively. The bilayer device shows high electron mobility that is about 6 times greater than that of the single layer device, which originated from highly ordering and increasing of grain size of F16CuPc thin films deposited on a DH-α6T quasi-mono layer.

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REFERENCES


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