

Improvement of Crystallinity for F₁₆CuPc Thin Film by DH- α 6T Quasi-monolayer

Rongbin Ye, Yuya Sasaki

Abstract— In this paper, we have reported on improvement of crystallinity for fluorinated copper phthalocyanine (F₁₆CuPc) thin film by an α,α' -dihexylsexithiophene (DH- α 6T) quasi-monolayer. By the detailed XRD and SEM analysis, highly ordering α -F₁₆CuPc thin films could be deposited on SiO₂/Si substrates modified by a DH- α 6T quasi-monolayer. The F₁₆CuPc/DH- α 6T TFT worked in hole-enhancement and electron-depletion modes with their hole and electron mobilities of 4.10×10^{-2} cm²/Vs and 2.19×10^{-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- α 6T 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 semiconducting properties are exploited for applications such as thin film transistors (TFTs), light emitting diodes, solar cells and gas sensors. [1-15] F₁₆CuPc 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 F₁₆CuPc TFTs were improved utilizing DH- α 6T 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 F₁₆CuPc exhibit typical ambipolar conduction. In this study, we report on improvement of crystallinity for F₁₆CuPc thin film by DH- α 6T quasi-monolayer and simultaneously formation of organic ambipolar pn heterojunction TFT.

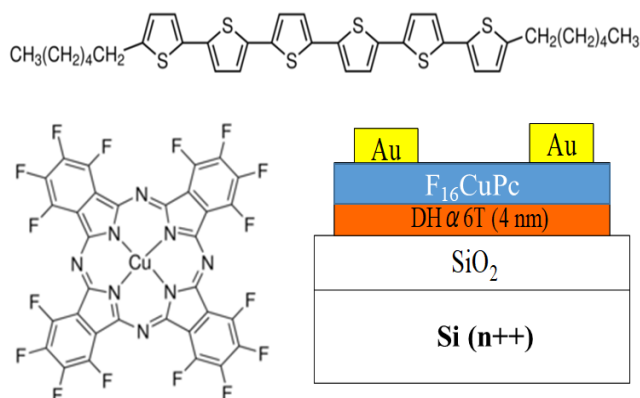
II. EXPERIMENTAL DETAILS

Figure 1 shows the chemical structures of DH- α 6T and F₁₆CuPc, and the schematic structure of organic TFT. Heavily n-doped Si substrate acts as the gate electrode with a 300 nm thermally grown SiO₂ layer (C_i ~ 10 nF/cm²) as the gate dielectric. The sample of DH- α 6T and F₁₆CuPc were purchased from Sigma Aldrich. DH- α 6T thin film of approximately 5 nm thickness (first layer) and F₁₆CuPc 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 1×10^{-3} 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 μ 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 CuK α radiation ($\lambda=1.54$ Å), operating in the Θ -2 Θ 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 μ m and a force constant of 0.12 N/m.

Figure1 Chemical structures of F₁₆CuPc and DH- α 6T, and schematic structure of organic ambipolar pn heterojunction TFT



III. RESULTS AND DISCUSSION

In Fig. 2(a), the typical XRD patterns of DH- α 6T thin film of 5 nm with d_{001} spacing of 3.34 nm ($2\Theta = 2.64^\circ$) was observed, and DH- α 6T molecules are standing up with respect to substrate surface. Figure 2(b) shows XRD patterns of F₁₆CuPc thin films of 20 nm deposited on SiO₂/Si substrate at 120 °C. Only a-form F₁₆CuPc with the 200 plane spacing $d_{200} = 1.43$ nm is observed [3]. The two XRD peaks correspond to (200) and (400) reflections. The XRD pattern of F₁₆CuPc films deposited on DH- α 6T quasi-monolayer modified SiO₂/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_{200} (1.41 nm) is slightly smaller than that of DH- α 6T thin films deposited on SiO₂/Si substrates. [18] Moreover, the appearance of the eighth-order diffraction peak at 18.77° ($d_{080} = 0.472$ nm) further enhanced the high order of the vacuum deposited films.

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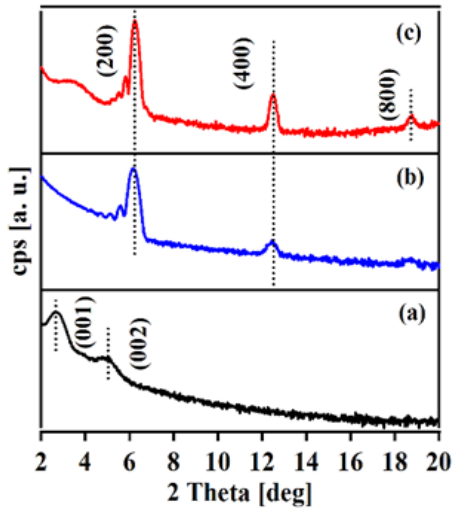


Figure 2 XRD patterns of (a) DH-α6T thin film of 5 nm, (b) an F₁₆CuPc single layer of 20 nm and (c) a 20 nm/5 nm of F₁₆CuPc/DH-α6T bilayer deposited on SiO₂/Si substrates at 120 °C.

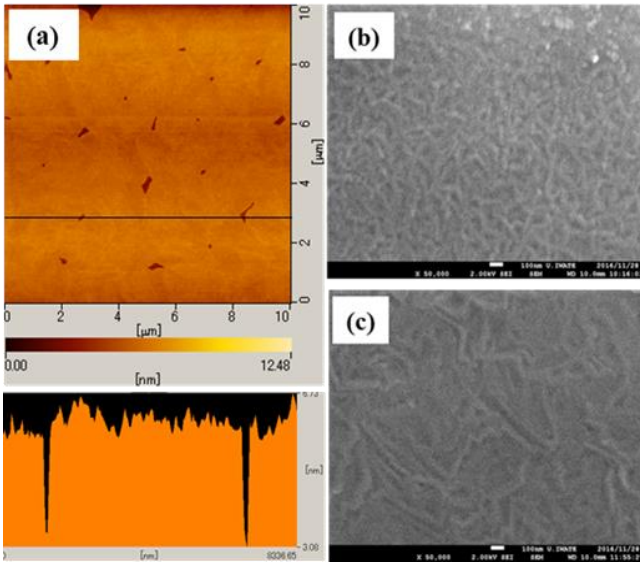


Figure 3 AFM images of (a) a DH-α6T of 5 nm with cross-sectional profile data corresponding to the black line, the SEM images of (b) the F₁₆CuPc single layer of 20 nm deposited on SiO₂/Si substrate and (c) the 20 nm/5 nm of F₁₆Pc/DH-α6T bilyer (All thin films deposited on SiO₂/Si substrates at 120 °C).

Figure 3(a) gives the height AFM image of a DH-α6T quasi-monolayer (~0.99 ML) deposited on SiO₂/Si substrate at 120 °C, and the nominal film thickness of is 5 nm. From the cross-sectional profile data corresponding to the black line in Fig. 3(a), the height of 1ML is about 3.1 nm, which agrees with the above-stated XRD data. Figs. 3b and 3c show the SEM images of the F₁₆CuPc thin film deposited on SiO₂/Si substrate and the F₁₆CuPc/DH-α6T thin film. The FWHM (0.169°) of the F₁₆CuPc/DH-α6T thin film is smaller than that (0.234°) of the F₁₆CuPc thin film in Fig. 2. This means that F₁₆CuPc molecules were crystallized better in the F₁₆CuPc thin film deposited on DH-α6T thin film. However, F₁₆CuPc molecules were randomly deposited on the amorphous SiO₂ substrate in the film forming process. As shown in Fig. 3(b), F₁₆CuPc molecules arrange on the substrate disorderly, lacking continuous. 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).

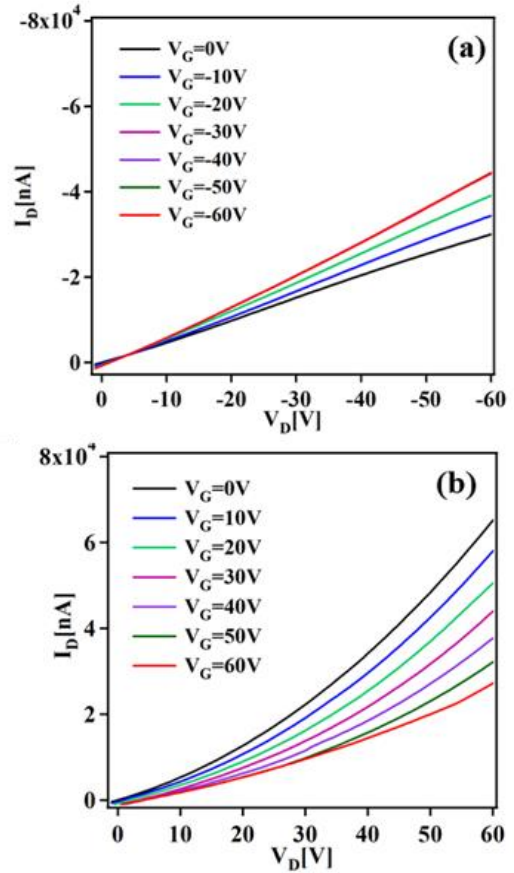


Figure 4 Output characteristics of F₁₆CuPc/DH-α6T TFT working in (a) hole-enhancement and (b) electron-depletion modes.

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] μ and V_T were extracted in the linear regime as followed:

$$I_D = \frac{W}{L} C_i \mu (V_G - V_T) V_D \quad (V_G \gg V_D), \quad (1)$$

where W , L , and C_i are the channel width, channel length, and gate dielectric capacitance per unit area, respectively. Hole and electron mobilities of $4.10 \times 10^{-2} \text{ cm}^2/\text{Vs}$ and $1.95 \times 10^{-2} \text{ cm}^2/\text{Vs}$, 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] Therefore, performance of the F₁₆CuPc/DH-α6T bilayer device could be expected to be improved by thermal annealing process.

Table I Summary of mobilities for the DH- α 6T quasi-monolayer, the F₁₆CuPc single layer and the F₁₆CuPc /DH- α 6T bilayer devices.

Active layer	μ_p (cm ² /Vs)	μ_n (cm ² /Vs)
DH- α 6T quasi-monolayer	2.99×10^{-2}	-
F ₁₆ CuPc single layer	-	3.56×10^{-3}
DH- α 6T/TiOPc bilayer	4.10×10^{-2}	1.95×10^{-2}

IV. CONCLUSION

In this study, we have reported on improvement of crystallinity for F₁₆CuPc thin film by a DH- α 6T quasi-monolayer. By the detailed XRD and SEM analysis, highly ordering α -F₁₆CuPc thin films could be deposited on SiO₂/Si substrates modified by a DH- α 6T quasi-monolayer. The F₁₆CuPc/DH- α 6T TFT worked in hole-enhancement and electron-depletion modes with their hole and electron mobilities of 4.10×10^{-2} cm²/Vs and 2.19×10^{-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- α 6T quasi-monolayer.

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