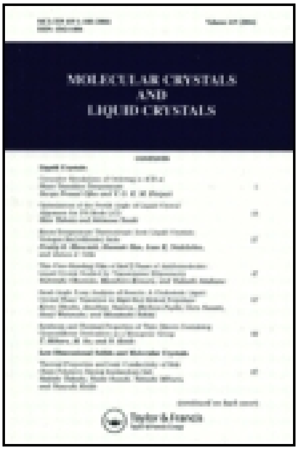

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On the Correlation between Morphology and Electronic Properties of Fluorinated Copper Phthalocyanine ($F_{16}CuPc$) Thin Films

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On the Correlation between Morphology and Electronic Properties of Fluorinated Copper Phthalocyanine (F_{16}CuPc) Thin Films

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We report on the correlation between morphology and electronic properties of fluorinated copper phthalocyanine (F_{16}CuPc) thin films deposited on SiO_2/Si substrates at different substrate temperatures. Highly ordered films with the 200 plane spacing of $d_{200} = 14.3$ Å is observed. Increasing the substrate temperature significantly improves the molecular ordering of F_{16}CuPc, and the smallest FWHM was gained at a substrate temperature of 120°C. The mobility is strongly dependent on the substrate temperature. Increasing in grain size at higher substrate temperatures improves the mobility of F_{16}CuPc TFTs, but gaps generated between grains degrade the performance of F_{16}CuPc TFTs at a substrate temperature higher than 110°C. When deposition of F_{16}CuPc is done at a substrate temperature of 100°C, the maximum mobility of 4.25×10^{-3} cm^2/Vs. can be obtained.

Keywords: F_{16}CuPc; field-effect mobility; morphology; organic thin film transistor

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1. INTRODUCTION

Organic semiconductors have been widely studied over the two last decades for their potential applications as thin film transistors (TFTs), light-emitting diodes (LEDs), and photovoltaic cells [1–5]. Among a variety of materials, phthalocyanines (Pcs) with high thermal and chemical stability represent one of the most promoting candidates for modern opto-electronic devices such as optical recording, organic LEDs, gas sensors, TFTs and solar cells [6–13]. Organic TFTs made from fluorinated copper phthalocyanine ($F_{16}CuPc$) led to an air-stable electron mobility of 0.03 cm^2/Vs, which is a promising material for n-channel operation [11]. On the other hand, the morphology and structure affect the performance of $F_{16}CuPc$ TFTs, which are very quite sensitive to growth conditions such as substrate temperature, deposition rate and type of the substrate [11,14–17]. Therefore, it is very important to control the growth parameters during growth of organic thin films.

In this work, we report on the correlation between morphology and electronic properties of $F_{16}CuPc$ thin film by X-ray diffraction (XRD), atomic force microscopy (AFM) and field-effect measurements. We also study the temperature dependence of the field-effect mobility for an $F_{16}CuPc$ TFT.

2. EXPERIMENTAL

$F_{16}CuPc$ (Fig. 1a) was purchased from Aldrich Chemical Co. and purified by sublimation twice at pressures of 3×10^{-2} Pa or lower. The schematic structure of the devices is shown in Figure 1b. A heavily n-doped Si substrate acts as the gate electrode with a 300 nm thermally grown SiO_2 layer ($C_i \sim 10\,nF/cm^2$) as the gate dielectric.

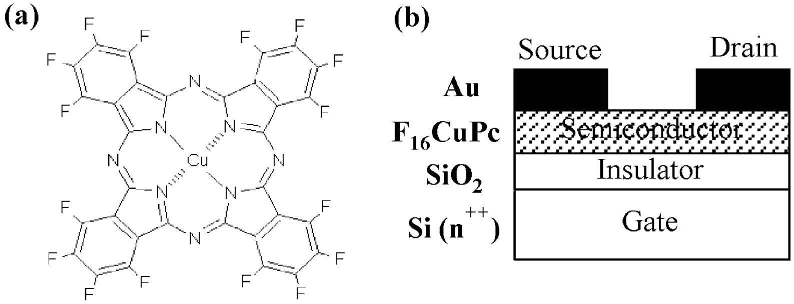


FIGURE 1 (a) Chemical structure of $F_{16}CuPc$ and (b) a schematic diagram of an $F_{16}CuPc$-based OTFT.

F_{16}CuPc thin films were deposited at various substrate temperatures (75, 100, 125 and 150°C, respectively) under a base pressure of less than 5×10^{-4} Pa. The substrate temperature was controlled by Digital Programming Regulator (KP1000, CHINO) with overshoot value less than 1°C and accuracy of ±0.2°C. Film thicknesses (ca. 30 nm) and growth rates (~0.2 Å/s) were monitored by a thickness and rate monitor (CRTM-6000, ULVAC). Finally, Au source and drain electrodes of ca. 100 nm were vacuum-deposited through a shadow mask with a channel width of 5 mm and lengths of from 50 to 70 μm. The characteristics of OTFTs were measured with a two-channel voltage current source/monitor system (R6245, ADVANTEST) under ambient laboratory air conditions. Temperature-dependence measurements were done by setting the device in a cryostat, which was temperature-controlled from 8.8 K to RT by a cryocooler using a He-gas flowing method.

The XRD analysis was performed on a diffractometer (Rint 2200 V, RIGAKU Co., Ltd.) with graphite monochromatized CuK_{α} radiation ($\lambda = 1.54$ Å). The morphology of the films was examined using the contact mode AFM (SPA 500, Seiko Instruments Co., Ltd.). The grain size

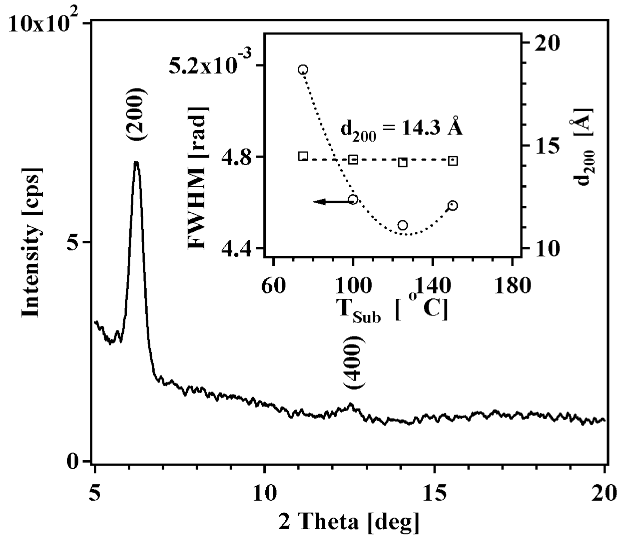
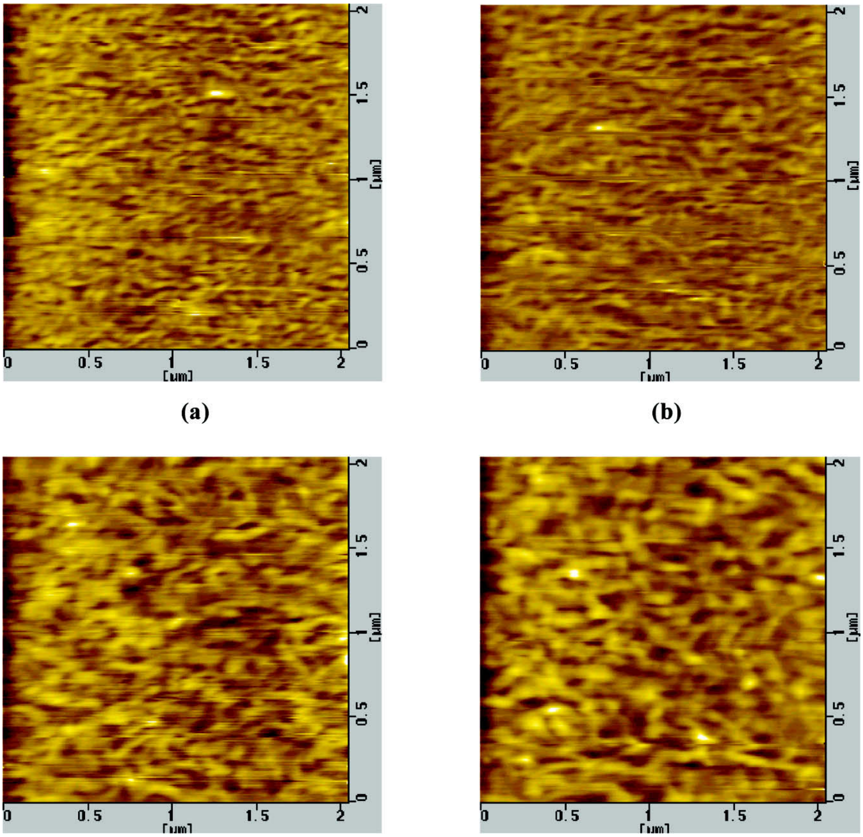


FIGURE 2 The XRD pattern of F_{16}CuPc thin films deposited at 125°C. The inset shows the effect of the substrate temperature on full width of half maximum (FWHM) of the (200) diffraction lines from F_{16}CuPc thin films deposited at 75, 100, 125 and 150°C.

and the RMS roughness were obtained by using AFM for each individual scan (2 μm × 2 μm).

3. RESULTS AND DISCUSSION

Figure 2 shows XRD spectra of F_{16}CuPc thin films deposited at a substrate temperature of 125°C. Only α-form F_{16}CuPc with the 200 plane spacing $d_{200} = 14.3$ Å (seen in the inset of Fig. 2) is observed [11]. The two XRD peaks correspond to (200) and (400) reflections. This is the signature of highly ordered films and the trace of the herringbone pattern parallel to the substrate. On the other hand, the inset of Figure 2



(a) (b) (c) (d)

FIGURE 3 AFM images of F_{16}CuPc thin films deposited at (a) 75, (b) 100, (c) 125 and (d) 150°C.

shows the full width at half maximum (FWHM) of the (200) diffraction line as a function of the substrate temperature (T_{Sub}). Increasing the substrate temperature significantly improves the molecular ordering of F_{16}CuPc and enhances crystallinity within the thin films, and the smallest FWHM was gained at $T_{Sub} = 120°C$.

The morphology of F_{16}CuPc films plays a critical role in determining their macroscopic semiconducting performance. Figure 3 shows the $2\,\mu m \times 2\,\mu m$ AFM topographic images of F_{16}CuPc thin films deposited at 75, 100, 125 and 150°C. For these F_{16}CuPc thin films, the growth of elongated bent strips that are lying parallel to the substrate surface can be observed. The length of the strips was evidently increasing for the higher substrate temperatures. As shown in Figure 4, the grain size and RMS increase with increasing the substrate temperature. The RMS roughness amplitude (σ) increases closely following an Arrhenius behavior as $\sigma \propto \exp(-E_{Bar}/k_BT)$ with the activation energy $E_{Bar} = 0.060\,\text{eV}$, and k_B is the Boltzmann constant in the inset of Figure 4 [18].

In Figure 5, the drain current is ploted as a function of the gate voltage under a drain voltage of 60 V for F_{16}CuPc TFTs deposited at

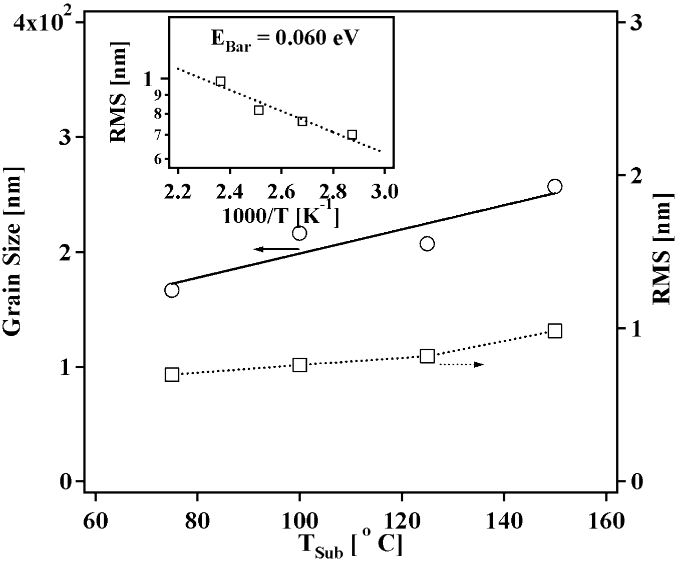


FIGURE 4 The RMS and grain size are shown as a function of substrate temperature of F_{16}CuPc thin films. The inset shows the RMS amplitude (σ) vs. inverse temperature (1000/T) with a linear fit yielding the activation barrier of $E_{Bar} = 0.018\,\text{eV}$.

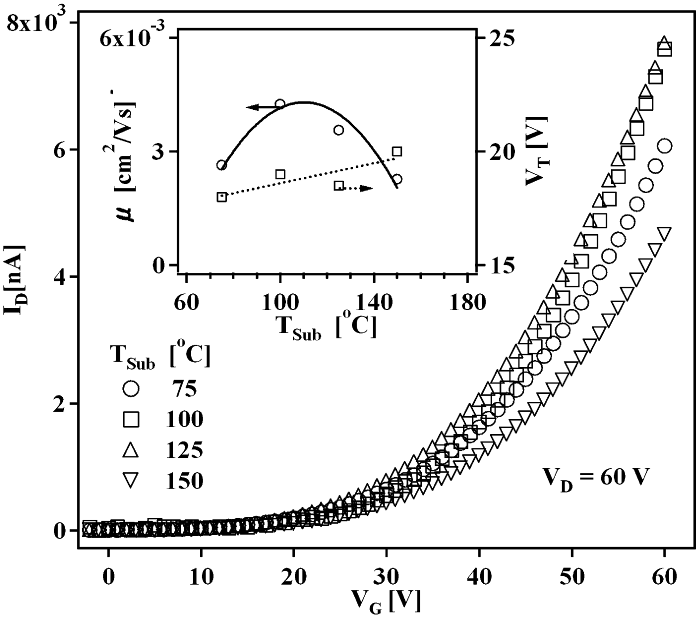


FIGURE 5 The drain current is ploted as a function of the gate voltage under a drain voltage of 60 V for $F_{16}CuPc$ TFTs deposited at 75, 100, 125 and 150°C. The inset shows the effects of substrate temperature on mobility and threshold voltage.

different substrate temperatures. The field-effect mobility (μ) and threshold voltage (V_T) of these OTFTs can be estimated using a standard analytic theory of MOSFET [19]. As shown in the inset of Figure 5, the mobility is strongly dependent on the substrate temperatures. Increasing grain size at high substrate temperatures improves electrical transport characteristics. On the other hand, gaps generated between grains degrade mobility of OTFTs at a substrate temperature higher than 110°C. When deposition of $F_{16}CuPc$ is done at a substrate temperature of 100°C, the maximum mobility of $4.25 \times 10^{-3}\,\mathrm{cm}^2/\mathrm{Vs}$ can be obtained.

Furthermore, Figure 6 shows an Arrhenius plot of the temperature dependence mobility for the $F_{16}CuPc$ TFT deposited at 125°C. At high temperatures (>140 K), the mobility is clearly thermally activated with thermal activation energy of $\Delta E = 0.039\,\mathrm{eV}$. At temperatures ranging from 50 K to 140 K, we have a second region with lower activation energy of $\Delta E = 0.010\,\mathrm{eV}$. Finally, for temperatures lower than 50 K, the mobility becomes practically temperature independent.

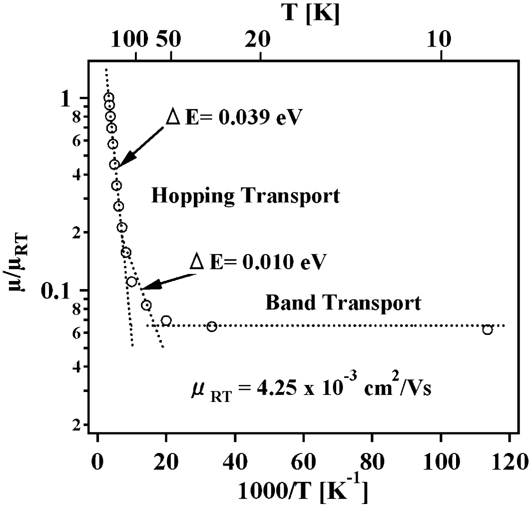


FIGURE 6 An Arrhenius plot of the temperature dependent mobility for the $F_{16}CuPc$ TFT deposited at 125°C.

These data could be explained by a mode where charge transport is limited by a high concentration at grain boundaries [20].

4. CONCLUSIONS

We have described a detailed characterization of the morphology and electrical properties of $F_{16}CuPc$ thin films deposited on SiO_2/Si substrates at different substrate temperatures. Highly ordered films with the 200 plane spacing of $d_{200} = 14.3\,Å$ is observed. The substrate temperature significantly affects the $F_{16}CuPc$ molecular ordering, and the smallest FWHM was gained at T_{Sub} of 120°C. The mobility is strongly dependent on the substrate temperature. Increasing in grain size at higher substrate temperatures improves electrical transport characteristics. On the other hand, gaps generated between grains degrade the mobility of $F_{16}CuPc$ TFTs at a substrate temperature higher than 110°C. When deposition of $F_{16}CuPc$ is done at a substrate temperature of 100°C, the maximum mobility of $4.25 \times 10^{-3}\,cm^2/Vs$. can be obtained.

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