Enhancing charge transport in copper phthalocyanine thin film by elevating pressure of deposition chamber

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Copper phthalocyanine (CuPc)-based thin film transistors were fabricated using CuPc films grown under different deposition pressure ($P_{\text{dep}}$) (ranging from $1.8 \times 10^{-4}$ Pa to $1.0 \times 10^{-1}$ Pa). The transistor performance highly depended on $P_{\text{dep}}$. A field-effect mobility of $2.1 \times 10^{-2}$ cm$^2$/V s was achieved under $1.0 \times 10^{-1}$ Pa. Detailed investigations revealed that $P_{\text{dep}}$ modulates the molecular packing and orientation of the organic films grown on a SiO$_2$/Si substrate and influences the charge transport. Furthermore, from a device physics point of view, contact resistance of the fabricated transistors decreased when $P_{\text{dep}}$ increased, which was beneficial in reducing energy consumption.

1. Introduction

Organic thin film transistors (OTFTs) have been the subject of intensive interest because of their applications in low-cost and large-area electronics [1,2]. Great efforts have been devoted to the improvement of device performance, which still remains one of the most critical issues in developing OTFTs. Generally, the optimization of molecular packing in the crystalline phase of organic semiconductors may facilitate charge hopping among the molecules, leading to the enhancement in electrical characteristics of OTFTs [3–6]. In the fabrication of OTFTs through vacuum deposition, the molecular packing in active thin films is usually optimized by regulating the temperature and surface properties of the substrate, since the weak van der Waals force among the organic molecules can be easily disturbed during the self-assembly process [7–10].

Recently, we observed that increasing deposition pressure ($P_{\text{dep}}$) modulated the orientation tendency of the deposited copper phthalocyanine (CuPc) molecules to be more perpendicular to the substrate, and the device performance of OTFTs was effectively enhanced [11]. However, the intrinsic correlation between the thin-film microstructure and the corresponding device performance is still lacking, to understand the relationship between these two phenomena is of great interest and significant importance for the improvement of device performance.

For organic semiconductors, it has been well documented that charge transfer between adjacent molecules can use a thermally activated hopping mechanism. Mobility obeys Arrhenius-type dependences [12]:

$$\mu = \mu_0 \exp \left( \frac{-E_a}{kT} \right).$$  

(1)

where $k$ is the Boltzmann constant, $T$ is the temperature, $\mu_0$ is the prefactor and $E_a$ is the activation energy. Combined with the Meyer–Neldel rule and the Gaussian
disorder model, the activation energy $E_a$ can be described as [13]:

$$E_a = \left[0.75 - 0.67 \log_{10} \left(\frac{n}{N}\right)\right] \sigma,$$

where $n/N$ is the relative carrier concentration, and $\sigma$ is the Gaussian density of states (DOS). For the same gate voltage, $V_g$, which means for the same effective $n/N$. Due to the different $\sigma$ the $E_a$ are different. So $\sigma$ can be used as an important material characterizing parameter for active organic semiconductor layers in OTFTs independent of the device geometry [14]. Moreover, in the perspective of the quantum-chemical calculations, charge transfer among molecules can be described by the Marcus theory [15,16].

Here, we thermally deposited CuPc in vacuum onto the SiO$_2$/Si substrates at different $P_{\text{dep}}$. Electrical performances of the fabricated OTFTs significantly improved when $P_{\text{dep}}$ was increased, exhibiting a field-effect mobility ($\mu_{\text{FET}}$) of 2.0 x 10$^{-2}$ cm$^2$/V s and an on/off ratio greater than 10$^5$. Investigations on the crystalline property of deposited CuPc films revealed that the molecular packing was modulated when $P_{\text{dep}}$ was increased. Therefore, the activation energy required for the charge hopping between adjacent molecules was reduced, and charge transport in the active layer was enhanced. Furthermore, the $Y$ function method clearly indicated that contact resistance ($R_C$) was lowered when $P_{\text{dep}}$ was increased.

2. Experimental

The CuPc with 99% purity was purchased from Aldrich and used without further purification. Fig. 1a illustrates the schematic structure of CuPc-based OTFTs, which is fabricated in the similar way to our recent report [11]. A heavily doped n-type (100) Si substrate with a 300 nm SiO$_2$ layer was cleaned in an ultrasonic bath successively using acetone, isopropyl alcohol, and deionized water. The substrates were placed in the chamber and maintained at 5 x 10$^{-5}$ Pa for 4 h. And then, the chamber pressure was adjusted by injecting high-purity nitrogen to be under a specific deposition pressure ($P_{\text{dep}}$, i.e., 10$^{-4}$, 10$^{-3}$, 10$^{-2}$, and 10$^{-1}$ Pa). The deposition rate for CuPc was kept as low as 0.08 Å/s, and the substrate temperature was maintained at 125 $^\circ$C during deposition. The thickness of resulting CuPc films were approximately 50 nm. Finally, a 50 nm Au electrodes were thermally deposited through a shadow mask. Therefore, the CuPc-based OTFTs had a bottom-gate top-contact architecture with the channel length ($L$) and width ($W$) of 50 and 500 $\mu$m, respectively.

The surface morphology and crystalline structure of the CuPc film were characterized by scanning electron microscopy (SEM, Hitachi S-4800, operating at 3 kV) and X-ray diffraction (XRD, Panalytical X’pert Pro X-ray diffractometer, Cu target, operating at 40 kV and 40 mA, $\lambda_{K\alpha 1} = 1.54056 \, \text{Å}$). The measurement of transistor characteristics was performed using a Keithley 4200-SCS semiconductor parameter analyzer. The measurements of the $I_d-V_g$ characteristics in the linear regime (at source–drain...
voltage $V_d = -10$ V) were conducted in 20 K temperature interval from 300 K to 180 K (Lake shore, CRX-4K). Each temperature step was maintained for 60 min to obtain thermal stabilization before the devices were measured.

To reveal the molecular packing influence on the molecular stacking and electronic properties of CuPc films, Marcus theory and the Einstein equation was performed. And the transfer integral and charge carrier mobility was estimated by density functional theory (DFT). A dimeric CuPc model was used with a fixed intermolecular distance, $r$, of 3.818 Å as a function of $d$-spacing. The B3LYP functional was chosen with effective core potential LANL2DZ basis sets for copper atom and the standard 6-31G(d,p) basis sets for nonmetal elements. All DFT calculations were done with the Gaussian 09 program package.

3. Results and discussion

The semiconducting small molecule of CuPc possesses good chemical and thermal stabilities even under ambient conditions, whereas difficulties in obtaining high electrical performance in transistor are typically encountered. The CuPc film also exhibited relatively low field-effect mobility ($\mu_{FET}$) in our CuPc-based OTFTs under $1.0 \times 10^{-4}$ Pa (Fig. 2a). The average value of $\mu_{FET}$ for the five devices on the same substrate is $1.1 \times 10^{-3}$ cm$^2$/V s (with a standard deviation of $0.2 \times 10^{-3}$ cm$^2$/V s), close to the reported one for the OTFTs prepared under similar condition [17]. Interestingly, the $\mu_{FET}$ increases to $5.2 \times 10^{-1}$ and $1.1 \times 10^{-2}$ cm$^2$/V s when $P_{\text{dep}}$ increases to $1.8 \times 10^{-3}$ and $2.4 \times 10^{-2}$ Pa, respectively. When the vacuum pressure is as high as $1.0 \times 10^{-1}$ Pa, this increasing trend in $\mu_{FET}$ is maintained, thereby reaching an average value of $2.0 \times 10^{-2}$ cm$^2$/V s. Moreover, the on/off ratio is also enhanced from $3 \times 10^3 (1.0 \times 10^{-4}$ Pa) to more than $10^5 (1.8 \times 10^{-1}$ Pa) (Table S1) by virtue of the improvement of on-current and the good maintenance of low off-current within the range $10^{-11} - 10^{-10}$ A. Furthermore, the TFTs based on CuPc films deposited under different $P_{\text{dep}}$ all exhibit good saturation behavior at high drain voltages ($V_d$), as seen in the output curves (Fig. 2b).

The threshold voltage ($V_{\text{th}}$) and sub-threshold swing (SS) are indicators for estimating the charge trap density at the interface between a semiconductor and an insulator. The small $V_{\text{th}}$ and SS values indicate low trap density. The maximum trap density ($N_{\text{trap}}$) can be calculated by using the following equation [18,19]:

$$N_{\text{trap}} \approx \left( \frac{q \log(e)}{kT} - 1 \right) \frac{C_i}{q}$$

where $q$ is the electronic charge, $k$ is Boltzmann constant, and $T$ is the temperature (300 K). $N_{\text{trap}}$ is estimated to be $6.1 \times 10^{12}$ cm$^{-2}$ at $1.0 \times 10^{-4}$ Pa and decreases to $5.0 \times 10^{11}$ cm$^{-2}$ at $1.8 \times 10^{-1}$ Pa (Table S1). The other prominent characteristics of CuPc-based OTFTs are the $V_{\text{th}}$ and SS tend to decrease with the increase of $P_{\text{dep}}$. These results indicate that high $P_{\text{dep}}$ for CuPc grown on the SiO$_2$ layer can effectively reduce the number of interface trap states, and then improves device mobility.

To improve device performance, efforts have been devoted to the modification of surfaces and optimization of active layers. In particular, the morphology and microstructure of the organic semiconductor have essential roles in mediating device performance [20–23]. In the current work, all the fabrication conditions were kept constant except $P_{\text{dep}}$ for the organic semiconductor. Therefore, the main factors affecting the observed performance enhancement are the grain sizes and molecular orientation in CuPc films at different vacuum pressures.

In our previous work, we observed an increase in grain size from 180 nm to 300 nm when the vacuum pressure for organic material deposition was changed from $1.0 \times 10^{-4}$ Pa to $1.8 \times 10^{-1}$ Pa [11]. Considering that the deposition rate for CuPc films was relatively high (0.2 Å/s), we speculated that increase in grain size can be attributed to sufficient mobility from an abundant dynamic energy when the CuPc molecules reached the substrate surface [24,25]. Thus, we deposited the CuPc for the devices in the current work under a much lower rate of 0.08 Å/s. As expected, the grain sizes were nearly identical for different vacuum pressures (Fig. 1b). By averaging the length of the long axis from 30 grains, the grain sizes had identical values even with increasing $P_{\text{dep}}$. Subsequently, we concentrated our investigation on the influence of molecular orientation in CuPc films on SiO$_2$ substrate.

XRD measurements were performed to investigate the crystalline property of CuPc films on SiO$_2$ substrate with different $P_{\text{dep}}$ (Fig. 3a). The films consist of only one phase ($\alpha$-CuPc) with three major reflections of (h 0 0) planes, with the $b$ axis as the high-charge transport direction.

![Fig. 2. (a) Transfer and (b) output characteristics among CuPc-based OTFTs prepared on SiO$_2$ under different $P_{\text{dep}}$.](image-url)
Using a peak fitting method, shoulder peaks were observed to verify the structure of the semiconductor in the conducting channel near the CuPc/SiO₂ interface. Both the main diffraction peaks (2 0 0) and the shoulder peaks shift to low angle with increasing $P_{\text{dep}}$. We calculated the vertical layer $d$-spacing of the CuPc molecular packing, which increased from 13.199 Å under 1.0 × 10⁻⁴ Pa to 13.522 Å under 1.8 × 10⁻¹ Pa (Fig. 3b, Table S1). Our previous results reveal that the collision probability between CuPc and N₂ molecules can be largely enhanced by increasing the chamber pressure, and CuPc molecule has the tendency to be standing up on the substrate [11].

For organic semiconductors based on $\pi$-conjugated small molecules, at the microscopic level, one of the major parameters governing the transport properties is the transfer integral ($t$) between adjacent molecules. $t$ is greatly sensitive to the molecular packing, that is, to the orbital overlap between the adjacent molecules. Highly $\pi-\pi$ stacking molecules can greatly increase the $t$, and then increase the mobility [26,27]. In order to further reveal the influence of packing structure on charge-transfer properties, we theoretically calculate the $t$ of CuPc dimer with a fixed the intermolecular distance ($r$) of 3.818 Å and changed $d$-spacing, the calculation results are shown in Fig. S1. It indicates that, as the $d$-spacing increases CuPc molecules become more $\pi-\pi$ stacking, the mobility of CuPc-based OTFTs increased.

To study the intrinsic charge transport in CuPc films, temperature-mobility dependence was characterized. For the devices deposited at different $P_{\text{dep}}$, $\mu_{\text{FET}}$ extracted from different gate voltages ($V_g$) all exhibited decreasing trends when the temperature was lowered (Fig. 4a). The data can be fitted well into straight lines in the plot of $\mu_{\text{FET}}$ versus $1/T$, which indicates that $\mu_{\text{FET}}$ follows Arrhenius-type dependences [28–30]. When the device characteristics were measured at a constant $V_g$ of −60 V, which means for the same effective carrier concentration, the reduced $E_a$ for the CuPc film grown at higher $P_{\text{dep}}$ is observed. It is a direct evidence for the reduced energetic disorder in this film (Fig. S2). Measured at different $V_g$, concomitantly at the charge carrier densities induced by different gate electrical fields, these Arrhenius plots intersect at the finite isokinetic temperature ($T_0$), which indicates that the Meyer–Neldel rule is dominant. Thus, charge carriers hop among disordered CuPc molecule matrices at the conducting channel.

The isokinetic temperature $T_0$ can be used to calculate the Meyer–Neldel energy $E_{\text{MN}}$ ($E_{\text{MN}} = k_B T_0$) and the width of the Gaussian density of states $\sigma$ ($\sigma = 5/2 E_{\text{MN}}$), which are parameters for the evaluation of disorder level of organic thin films [14]. The extrapolation of the fitting lines intersect at the isokinetic temperatures $T_0 = 1141, 1022, 950$ and 869 K for CuPc deposited at $P_{\text{dep}}$ range of 1.0 × 10⁻⁴ Pa to 1.8 × 10⁻¹ Pa. Consequently, the corresponding $E_{\text{MN}}$ decreased from 98.3 meV to 74.8 meV and $\sigma$ reduced from 245.7 meV to 187.1 meV (Fig. 4b, Table S1). The value of $\sigma$ determines the disorder level of films at the interface with gate insulators where charge transport takes place [31,32].
The Gaussian density of states, $\sigma$, is determined by a van der Waals component ($\sigma_{vdw}$) and a dipolar component ($\sigma_d$) [33]:

$$\sigma = (\sigma_{vdw} + \sigma_d)^{1/2},$$  \hspace{1cm} (4)

And the dipolar component is described as [34]:

$$\sigma_d = \frac{7.04 c^{1/2} p}{\rho^{2/3}}.$$  \hspace{1cm} (5)

where $c$ is the fraction of lattice sites occupied by dipoles, $p$ is the dipole moment, $\rho$ is the intersite distance, $\epsilon$ is the dielectric constant. $\sigma_d$ is governed by the permanent dipoles. Note that CuPc molecule has a $D_{2h}$ symmetry structure with atoms vibrating in a plane. Thus $p = 0$, $D$, resulting in that $\sigma_d$ can be neglected. Since $\sigma_{vdw}$ is defined by a charge-induced dipolar interaction, lower value indicates enhanced $\pi-\pi$ stacking among molecules. Consequently, the results presented in Fig. 4b imply that higher chamber pressure can improve the charge transports in the CuPc films by optimizing the molecular stacking.

Furthermore, our proposed method also shows its advantage from the perspective of device physics. We applied the Y function method to calculate $R_C$ and low-field mobility ($\mu_0$) (Fig. S3) [35,36]. For the devices with CuPc deposited from low to high $P_{dep}$ (Fig. 5), the calculated $R_C$ remarkably decreased from 0.91 MΩ cm to 0.11 MΩ cm (Table S1). Thus, the decrease in $R_C$ at high $P_{dep}$ may result in a reduction in energy consumption. Moreover, $\mu_0$, which characterizes the intrinsic carrier mobility excluding the influence of $R_C$, improved from 2.0 $\times$ 10$^{-3}$ to 2.3 $\times$ 10$^{-2}$ cm$^2$/Vs (Table S1) when $P_{dep}$ increased. This observation is also an indication of the enhanced organic thin film property in OTFTs, which resulted from the increase in $P_{dep}$ for CuPc deposition.

4. Conclusions

CuPc films were prepared on SiO$_2$ substrates under different $P_{dep}$ ranging from 1.0 $\times$ 10$^{-4}$ Pa to 1.8 $\times$ 10$^{-1}$ Pa. The CuPc-based OTFTs exhibited improved performance when the pressure was increased. XRD results and measurements of temperature-dependent mobility revealed that the charge transport in the active layer was enhanced at higher $P_{dep}$. Moreover, $R_C$ reduced and calculated $\mu_0$ value increased when $P_{dep}$ increased, indicating improved film property. This study provides an in-depth discussion of the relationship between the modified molecular packing and the corresponding enhanced charge transport, under a convenient vacuum deposition approach, which is of great importance. Besides, there is still a space to further improve device performance by interface engineering techniques, which can reduce the defect density at the organic/dielectric interface and can enhance the charge injection at the organic/metal one.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.orgel.2014.05.010.

References