

Improved mobility of zinc hexadecafluorophthalocyanine (ZnPcF₁₆) thin film transistors using *p*-6p as the inducing layer

YINGLI SUN, SHIRONG WANG^a, XIANGGAO LI^a, FENG MA^{*}

School of Chemistry and chemical Engineering, Tianjin University of Technology, Tianjin 300384

^a*School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, PR China*

The n-type organic thin film transistors (OTFTs) employing zinc hexadecafluorophthalocyanine (ZnPcF₁₆) as the active layer and para-hexaphenyl (*p*-6p) as the inducing layer have been demonstrated. Compared with the ZnPcF₁₆-based OTFTs without the *p*-6p inducing layer, the charge carrier field-effect mobility (μ) of the ZnPcF₁₆/*p*-6p OTFTs is greatly improved. The mobility of the ZnPcF₁₆/*p*-6p OTFTs is $1.30 \times 10^{-2} \text{ cm}^2/\text{V}\cdot\text{s}$. The improved performance is attributed to the introduction of *p*-6p to form a highly oriented and continuous film of ZnPcF₁₆ with the molecular π - π stack direction parallel to the substrate.

(Received July 10, 2015; accepted September 9, 2015)

Keywords: Thin film transistors, Organic semiconductors, Fluorinated zinc phthalocyanine, Grain boundaries

1. Introduction

Organic thin-film transistors (OTFTs) employing organic semiconductors as the active layer have received widely studies because of their potential application in displays, logic circuits, and sensors [1-4]. To date, the performance of p-type pentacene-based OTFTs has reached the level of a-Si devices [5]. Compared with p-type materials, the mobility of the n-type materials with high air stability is relatively low [6]. Therefore, how to improve the mobility of n-type materials becomes a challenge to meet the requirements of practical applications. Zinc hexadecafluorophthalocyanine (ZnPcF₁₆, shown in Fig. 1) is one of a few air-stable n-type organic semiconductors with a low electron field-effect mobility. To improve the performance of ZnPcF₁₆-based OTFTs, Bao *et al.* [7] have prepared transistors at different substrate deposition temperatures (T_d). The highest electron mobility of $1.2 \times 10^{-3} \text{ cm}^2/\text{V}\cdot\text{s}$ is obtained at a higher T_d of 215°C. Jiang *et al.* [8] have reported ZnPcF₁₆-based organic single-crystal field-effect transistors with a higher mobility about $1.1 \text{ cm}^2/\text{V}\cdot\text{s}$. Highly oriented and continuous organic thin film is an ideal active layer to improve their device performance [9]. However, their thin films are normally composed of needle-like crystals with random orientations, which will induce more grain boundaries. The high defect concentration in grain boundaries of multi-crystal thin films usually leads to poor carrier transport, especially for phthalocyanine compounds [9-11].

In this study, we employ para-hexaphenyl (*p*-6p,

shown in Fig. 1) as the inducing layer to form well-organized ZnPcF₁₆/*p*-6p thin films by physical vapor deposition technique. The morphology and structure of these thin films are examined by XRD and SEM. Furthermore, we fabricate ZnPcF₁₆/SiO₂ and ZnPcF₁₆/*p*-6p OTFTs and compared their electrical characteristics to illustrate the significant role of *p*-6p in the improvement of device mobility.

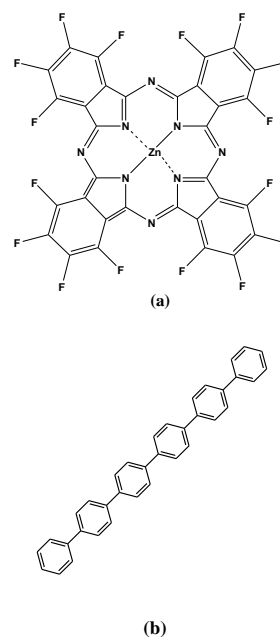


Fig. 1. Molecular structure of (a) ZnPcF₁₆ and (b) *p*-6p.

2. Experimental

The device configurations are given in Fig. 2. In the fabrication of the ZnPcF₁₆/*p*-6p organic films and OTFTs, a heavily doped, *n*-channel Si wafer was used as the gate electrode and substrate, with a 300 nm thermally oxidized SiO₂ layer as the gate insulator. ZnPcF₁₆ and *p*-6p were purified twice by thermal gradient sublimation prior to processing. Firstly, *p*-6p was deposited on SiO₂ at a substrate temperature of 180 °C, carefully controlling the thickness 6 nm. Subsequently, a 7 nm ZnPcF₁₆ layer was deposited on the *p*-6p thin film. All organic films were deposited in vacuum (10⁻⁴–10⁻⁵ Pa) at a rate of 0.5 nm min⁻¹. In fabrication of the ZnPcF₁₆/*p*-6p OTFTs, the ZnPcF₁₆/*p*-6p films on the wafer substrate were rapidly moved to another vacuum chamber (10⁻⁴ Pa) for defining the source and drain electrodes by thermal evaporation of Au with a shadow mask. The width and length of the channel were 6000 μm and 200 μm, respectively. The ZnPcF₁₆/SiO₂ films and OTFTs were fabricated at the same conditions without introducing the *p*-6p organic layer. The transfer characteristics of the two transistors were measured with two Keithley 236 source-measurement units under ambient conditions at room temperature.

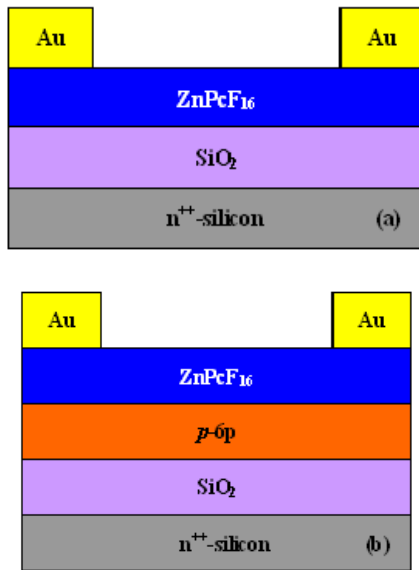


Fig. 2. The device configurations of (a) ZnPcF₁₆/SiO₂ and (b) ZnPcF₁₆/*p*-6p thin film transistors

3. Results and discussion

Fig. 3 shows the XRD pattern of the ZnPcF₁₆/SiO₂ and ZnPcF₁₆/*p*-6p thin films. The X-ray diffraction was performed in a Rigaku D/max 2500 PC X-ray diffractometer with a Cu Kα radiation ($\lambda = 1.54056 \text{ \AA}$). The diffraction peaks of the ZnPcF₁₆/SiO₂ film peak at $2\theta = 6.18$, corresponding to d_{200} spacing of 14.29 Å, is observed.

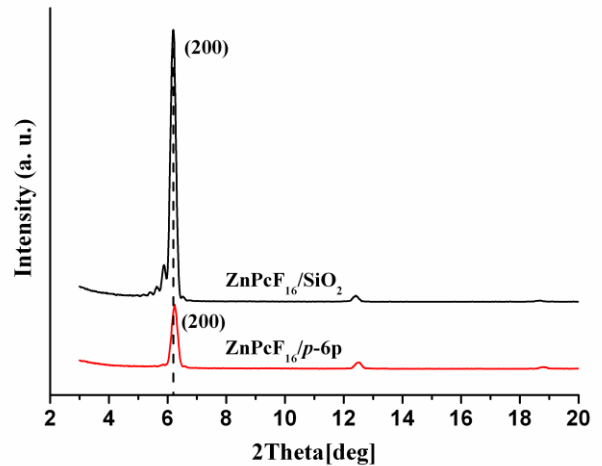


Fig. 3. X-ray diffraction spectra of ZnPcF₁₆/SiO₂ and ZnPcF₁₆/*p*-6p thin films

The result indicates that ZnPcF₁₆ molecules are grown upright on the SiO₂ substrate with the metastable α -phase [7, 10, 12]. For ZnPcF₁₆/*p*-6p film, a sharp peaks at $2\theta = 6.24$, $d_{200} = 14.15 \text{ \AA}$, have a slight deviation from the diffraction peak of ZnPcF₁₆/SiO₂ thin film. It possibly originates from the difference between molecule-substrate interaction and intermolecular interaction [10]. These results also demonstrate that the ZnPcF₁₆ molecules are approximately standing-up on the *p*-6p layer.

Fig. 4 shows the SEM of ZnPcF₁₆/SiO₂ and ZnPcF₁₆/*p*-6p thin films. The SEM images were obtained by a FEI Nanosem 430 electron microscopy instrument. The surface image of ZnPcF₁₆/SiO₂ thin film is showed in Fig. 4a. The ZnPcF₁₆ molecules arrange on The FWHM of the ZnPcF₁₆/SiO₂ thin film is smaller than that of the ZnPcF₁₆/*p*-6p thin film in Fig. 3. This means that ZnPcF₁₆ molecules were crystallized better in the ZnPcF₁₆/SiO₂ thin film. However, ZnPcF₁₆ molecules were randomly deposited on the amorphous SiO₂ substrate in the film-forming process. As shown in Fig. 4(a), ZnPcF₁₆ molecules arrange on the substrate disorderly, lacking continuous. The growth behavior of the *p*-6p thin film has been studied systematically [13]. A highly-ordered large-sized and smooth *p*-6p ultrathin film can supply a high quality substrate (the inducing layer) for the growth of phthalocyanine molecules. ZnPcF₁₆ molecules can be oriented after the employment of the *p*-6p inducing layer. The image of the ZnPcF₁₆/*p*-6p film shows a strip grain pattern in Fig. 4(b). The π - π stack direction of ZnPcF₁₆ molecules in the ZnPcF₁₆/*p*-6p thin film is parallel to the *p*-6p layer, which will facilitate the carrier transportation. Compared with the image of the ZnPcF₁₆/SiO₂ film, the ZnPcF₁₆/*p*-6p thin film shows higher order, fewer grain boundaries and traps in the ZnPcF₁₆ bulk. The highly oriented and continuous organic semiconductor thin film will lead to an improvement in the charge transport of organic electronic devices.

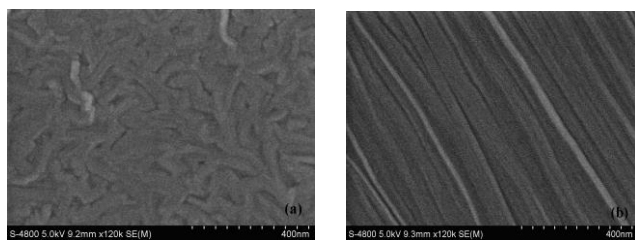


Fig. 4. SEM images of (a) ZnPcF₁₆/SiO₂ and (b) ZnPcF₁₆/p-6p thin film

Fig. 5(a) and Fig. 5(b) show the typical transfer characteristics of the ZnPcF₁₆/SiO₂ and ZnPcF₁₆/p-6p OTFTs with different gate voltages at a fixed V_D of 100 V. The field effect mobility were extracted from figure Fig. 5a and Fig. 5b in the saturation region ($V_G \geq (V_G - V_T)$) based on

$$I_{DS} = \frac{W}{2L} \mu C_i (V_G - V_T)^2 \quad (1)$$

Where I_{DS} is the drain-source current, W and L are the width and length of the channel, respectively, μ is the field-effect mobility, V_G is the gate voltage and V_T is the threshold Voltage. The capacitance per unit area of the insulator (C_i) is 8 nF/cm².

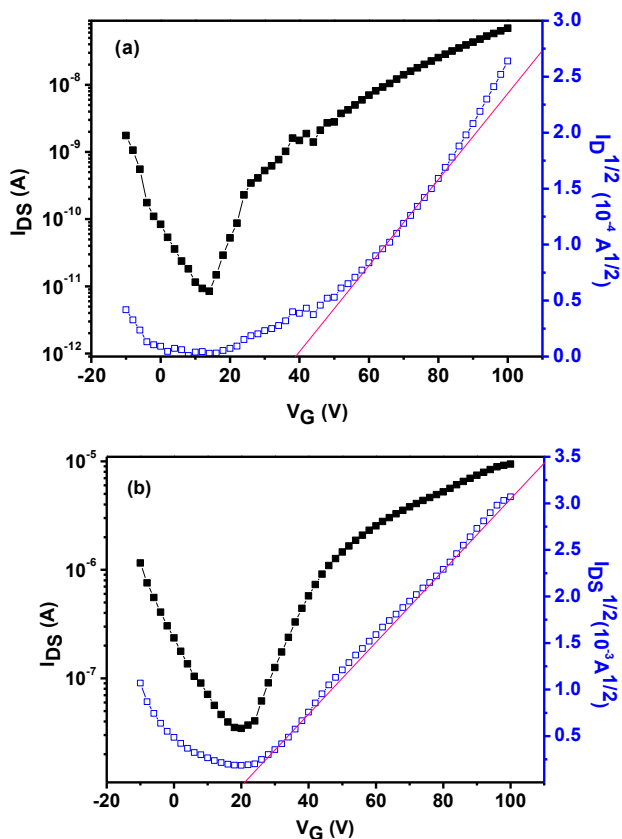


Fig. 5. Transfer curves characteristics of (a) ZnPcF₁₆/SiO₂ and (b) ZnPcF₁₆/p-6p thin film transistors

From the transfer characteristics, we extract a mobility μ of 0.60×10^{-4} cm²/V s for ZnPcF₁₆/SiO₂ transistors while a mobility μ of 1.30×10^{-2} cm²/V s for ZnPcF₁₆/p-6p device. The mobility of ZnPcF₁₆/p-6p thin film transistor has been greatly improved due to the employment of the p-6p inducing layer leading to the formation of the high-quality ZnPcF₁₆ film.

4. Conclusion

In summary, highly oriented thin film of ZnPcF₁₆ with the molecular π - π conjugated directions parallel to the substrate has been prepared. By applying this film-forming technique, the mobility of the n-channel ZnPcF₁₆/p-6p OTFTs is greatly improved. Employing p-6p as the inducing layer is an effective and simple method to fabricate high performance OTFTs for practical applications.

Acknowledgements

The authors are grateful to Donghang Yan research group in Changchun Institute of Applied Chemistry of Chinese Academy of Sciences for support of devices' fabrication. The work has been partially supported by National Natural Science Foundation of China (no. 21401138) and High School Science and Technology and Technology Fund Planning Project of Tianjin (no. 20130508).

References

- [1] R. Ye, M. Baba, K. Suzuki, K. Mori, Thin Solid Films **517**, 3001 (2009).
- [2] Y. C. Hu, G. F. Dong, L. D. Wang, Y. Liang, Y. Qiu, Chin. Phys. Lett. **21**, 723 (2004).
- [3] J. H. Yang, M. Degawa, K. S. Song, C. Wang, H. Kawarada, Mater. Lett. **64**, 2321 (2010).
- [4] S. Y. Yu, M. D. Yi, D. G. Ma, Chin. Phys. Lett. **25**, 755 (2008).
- [5] T. N. Jackson, Y. Y. Lin, D. J. Gundlach, H. Klauk, IEEE J. Sel. Top. Quantum Electron. **4**, 100 (1998).
- [6] F. Ma, S. R. Wang, X. G. Li, D. Yan, Chin. Phys. Lett. **28**, 118501 (2011).
- [7] Z. Bao, A. J. Lovinger, J. Brown, J. Am. Chem. Soc. **120**, 207(1998).
- [8] H. Jiang, J. Ye, P. Hu, F. X. Wei, K. Z. Du, N. Wang, T. Ba, S. L. Feng, C. Kloc, Sci. Rep., **4**, 7573 (2014).
- [9] H. Wang, F. Zhu, J. Yang, Y. Geng, D. Yan, Adv. Mater. **19**, 2168 (2007).
- [10] Z. Bao, A. J. Lovinger, A. Dodabalapur, Adv. Funct. Mater. **9**, 42 (1997).
- [11] J. Zhang, H. Wang, D. Yan, Appl. Phys. Lett. **84**, 142 (2004).
- [12] H. Wang, J. Wang, H. Huang, X. Yan, D. Yan, Org. Electron. **7**, 369 (2006).
- [13] J. Yang, T. Wang, H. Wang, F. Zhu, G. Li, D. Yan, J. Phys. Chem. B **112**, 3132 (2008).

*Corresponding author: mafontune@sina.com.cn