

Comparative study on different annealing methods and choice of solvent in organic field effect transistors based on Poly(3-hexylthiophene)

C.L. CHUA, K.L. WOON*

Low Dimensional Materials Research Center, Department of Physics, Faculty of Science, University of Malaya, 50603 Kuala Lumpur, Malaysia

A simple approach to study the effect of processing on the charge carrier mobility in an organic field effect transistor (OFET) based on regioregular poly(3-hexylthiophene) (RR P3HT) is investigated in this paper. It is found that different processing conditions can induce different degrees of hysteresis, which is well correlated with the charge mobility where lower hysteresis represents higher stability and hence higher charge mobility. Solvent annealing tends to create large nano-scale pinholes in P3HT which degrade the mobility.

Keywords: *organic field effect transistor; regioregular poly(3-hexylthiophene); solvent annealing; thermal annealing*

© Wrocław University of Technology.

1. Introduction

Organic field effect transistors (OFETs) with conjugated polymer as an active layer have drawn interest due to their simplicity and flexibility in processing as well as low cost electronic applications [1–3]. Despite the attractive advantages, the performance of OFETs has still been hindered by ease of degradation due to exposure to air. This results in lower field-effect mobility and high operating voltage [4–6]. The charge carrier mobility of active material is vital in determining the performance of OFETs [7]. Research towards highly air-stable and more robust materials is extremely important for the improvement of the performance of OFETs. Regioregular poly(3-hexylthiophene) (RR P3HT) remains one of the most promising materials for the fabrication of OFETs due to its solution processability, good self-organizing properties and ability to form crystalline structure suitable for electronic applications [8].

Researchers have shown that RR P3HT exhibits high field-effect mobility [8]. The mobility reported is strongly dependent on the structural or-

dering of the thin film and thus on the film forming process. Spin coating [9], drop casting [10], dip casting are common techniques in processing RR P3HT [11]. Special techniques such as slide coating reduce the cost of device processing [12]. These film forming techniques have its own advantages in improving certain properties such as mechanical strength, crystallization and alignment of the RR P3HT conjugated backbones [13]. In addition, the films prepared from different choices of solvents [7] and post processing treatments such as thermal annealing [9] and solvent annealing [13] can result in a highly ordered or highly crystalline film for field-effect transport. Generally, solvent with higher boiling point and with slower evaporation rate promotes highly crystalline film resulting in higher charge mobility [10]. Solvent annealing is a technique that provides an environment in which the saturated vapor pressure induces self organization of molecules, resulting in higher crystallization. Although a lot have been done on the solvent annealed films of P3HT:PCBM for solar cell applications, few researches have studied the effect of solvent annealing on the performance of OFETs [14]. Therefore, further studies are required

*E-mail: ph7klw76@um.edu.my

to understand the phenomena associated with this technique.

The most efficient charge transport in a polymer OFET occurs along the direction of intermolecular $\pi - \pi$ stacking within the crystalline domain [15, 16]. Therefore, higher degree of crystallinity and longer conjugation that induces the orientation of $\pi - \pi$ stacking P3HT molecules [13] are highly favorable. Besides, the connectivity between the crystalline domains is also attributed to the conductivity of the organic film and as a result promotes charge carrier transport in OFETs [10]. In this paper, we look into the effect of choice of solvent and annealing treatment on the molecular structures of RR P3HT utilizing spin coating techniques. Although a lot of studies have been done on the P3HT as polymer semiconducting component for OFETs, few researches have studied the impact of solvent annealing on thin film prepared from different solvents towards performance of molecular structure and thus the performance of OFET. Hence, the relationship between processing and molecular structural ordering is studied. Thus, we relate the process induced structural properties directly to the charge mobility in the transistor. Siringhaus et al. reported RR P3HT lamellae to exhibit two orientations depending on the processing conditions [6]. We have found that the field effect mobility can vary significantly in P3HT devices fabricated using different processing techniques. The crystallinity and morphology of P3HT thin films were studied using X-ray diffraction (XRD) and atomic force microscopy (AFM) respectively.

2. Experimental

A bottom-gated device architecture of RR P3HT based OFET was fabricated. The active material, RR P3HT, purchased from American Dye Source Inc, was dissolved in two different solvents as an active layer of the OFET. 1 wt. % solution prepared from chloroform (CF) and dichlorobenzene (DCB) was filtered through a 0.45 μm pore size nylon filter and deposited on 100 nm thermally grown oxide layer on Si/SiO₂ substrate via spin-coating to form a thin film. The substrate was cleaned with acetone, ethanol and deionized wa-

ter with the aid of ultrasonic agitation followed by nitrogen purge to get rid of dust particles prior to spin-coating. RR P3HT prepared from chloroform was then spin-coated at a speed of 1500 rpm for one minute while RR P3HT prepared from dichlorobenzene was spin-coated for 3 minutes, including pre-wetting process at a speed of 500 rpm for 5 second. It was then treated differently either by thermal annealing (TA) or solvent annealing (SA) to investigate the effect of post treatment on the thin film properties. For thermal annealing, the film was heated at 100 °C for 5 minutes. For solvent annealing, the sample was held in a container saturated with chloroform vapor for 60 minutes. Both films were about 80 nm thick. The conditions of processing are summarized in Table 1. The experiment was then followed by patterning 100 nm thick source and drain electrodes on the thin film via thermal vacuum evaporation, employing a shadow mask. The whole experiment was performed at room temperature under N₂ while the electrical characterization was done under ambient using two Keithley's 236 source measuring units.

Table 1. Summary of processing conditions of OFET devices fabricated either by solvent annealing (SA) or thermal annealing (TA) using dichlorobenzene (DCB) or chloroform (CF).

Device	Solvent	Post Treatment
1	CF	TA
2	CF	SA
3	DCB	TA
4	DCB	SA

3. Results and discussion

Output and transfer characteristics of the fabricated RR P3HT-based devices are shown in Fig. 1. All the devices exhibit hole transport behavior with mobility of $\sim 3.0 \times 10^{-4}$ to $\sim 1.7 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Devices with the films prepared from CF show the output characteristics more stable compared to those prepared from DCB. Higher hysteresis can be observed in the output characteristics of device 3

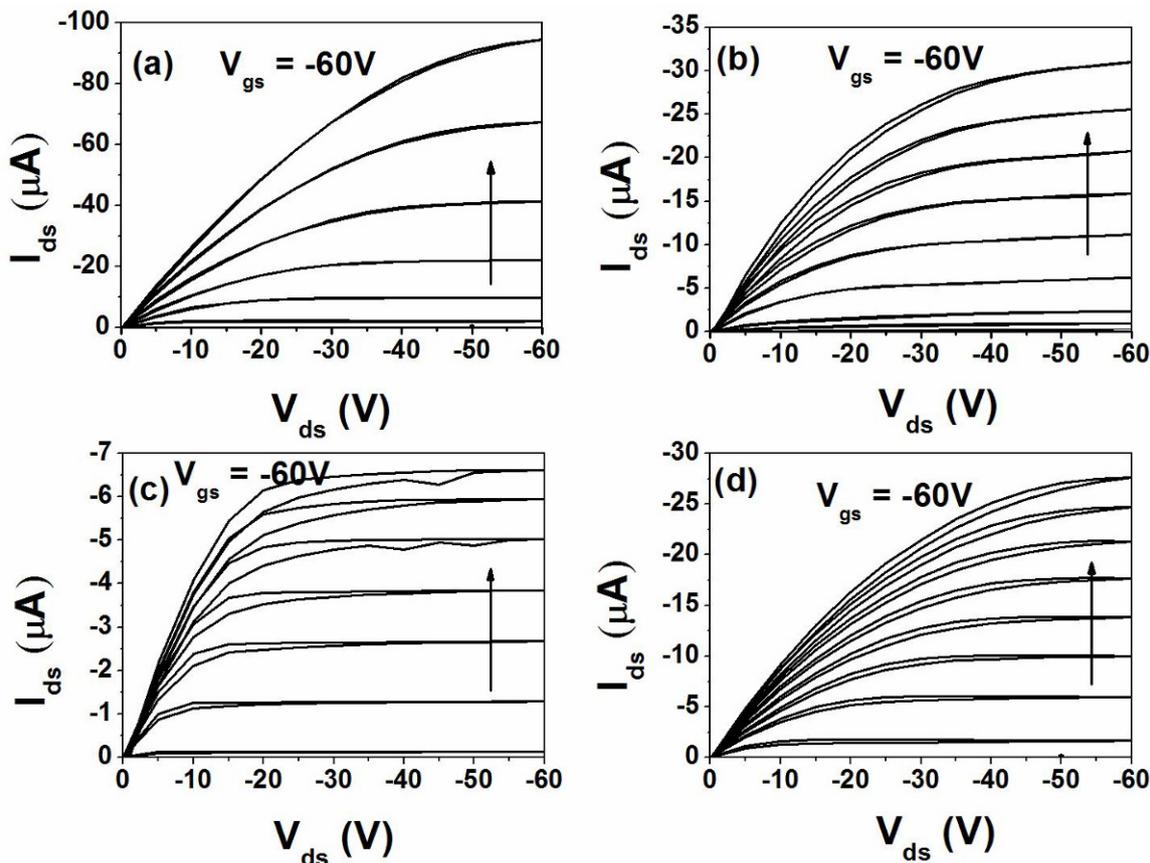


Fig. 1. Output characteristics of (a) device 1, (b) device 2, (c) device 3, and (d) device 4 at gate voltages from 0 to -60 V with an increment of -10 V indicated by the arrow.

(mobility = $0.3 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), and 4 (mobility = $1.8 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) rather than in device 1 (mobility = $17 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) and 2 (mobility = $5.2 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). This suggests higher stability in the performance of the devices prepared from CF compared to the devices made of the film prepared from DCB. For the devices of films prepared from CF, the thermal annealed device 1 with lower hysteresis gives better electrical characteristics than device 2, indicating that thermal annealing facilitates higher ordered structure of the film prepared from CF. However, hysteresis is higher for thermal annealed devices than for the solvent annealed devices made of the film prepared from DCB as illustrated in Fig. 1c and Fig. 1d for devices 3 and 4, respectively. The current density for device 3 is lower than for device 4. The degree of hysteresis is well correlated with the charge mobility where lower hys-

teresis represents higher stability and hence higher charge mobility. Significant difference in hysteresis behavior shown in the output characteristics is mainly attributed to the semiconductor bulk itself and thermal annealing which effectively decreased the charge trapping within the semiconductor bulk prepared from CF, hence reducing hysteresis. Transfer characteristics of the devices are shown in Fig. 2. The mobility was calculated at saturation regime from the $I_{ds}^{1/2} - V_{gs}$ curve at $V_{ds} = -60$ V for all the devices

Despite lower boiling point, the devices made of the films prepared from CF, both thermally and solvent annealed, clearly exhibit higher charge mobility than the devices made of the films prepared from DCB. It is hypothesized that the films prepared from CF induce higher ordered domains for charges to travel across the channel compared to the films prepared from DCB. This is strongly

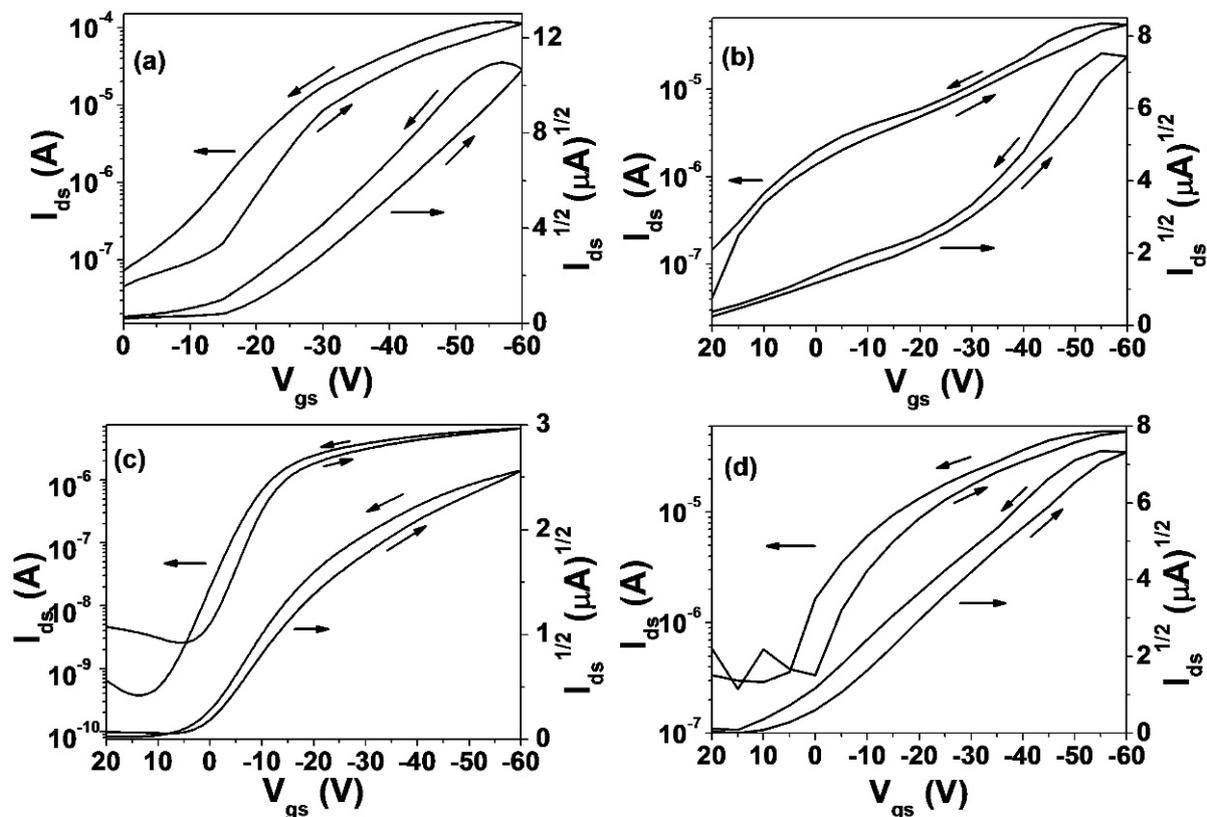


Fig. 2. Transfer characteristics of (a) device 1 (b) device 2 (c) device 3 (d) device 4 respectively. The upward and downward arrows indicate the direction of gate voltage sweep.

supported by the XRD (D5000, Siemens) results in Fig. 3. The XRD patterns confirm (100) Bragg's diffraction peaks corresponding to the main chain of lamellar structured P3HT with a lattice spacing of ~ 1.65 nm which is oriented parallel to the surface of dielectric layer. The corresponding (100) peak of device 1 at approximately $2\theta = 5.3^\circ$ is the highest among the devices, which is consistent with the highest charge mobility. The slightly weaker intensity of the peak for device 2 suggests poorer crystallinity of the film compared to device 1. Further we observe a shift of (100) peaks for device 2 and 4, which correspond to 1.49 nm and 1.55 nm, respectively compared to device 1, which is 1.66 nm, indicating denser packing. The (100) peak of device 2 and device 4 is still dominant suggesting higher crystallinity degree compared with device 3.

The presence of weaker (200) and (300) peaks in the XRD patterns implies the existence of long range order conjugated chain in the films. These peaks are only observable in devices 1 and 2 which are prepared from CF but not in devices 3 and 4 which are prepared from DCB. This indicates that the long range order of polymer chain strongly depends on the solvent used for device fabrication. A lower intensity of (100) peak in the XRD and distinct broad peak between (200) and (300), observable for device 3, imply lower crystallinity degree and chain defect within the polymer matrix. The distinct broad peak at 13.5° might be the result of superposition of two Gaussian peaks of (200) and (300) with large spread function, indicating certain degree of macroscopic orientational order but poorer microscopic order. The device prepared from chloroform suffered reduction in current density when subjected to solvent annealing as shown

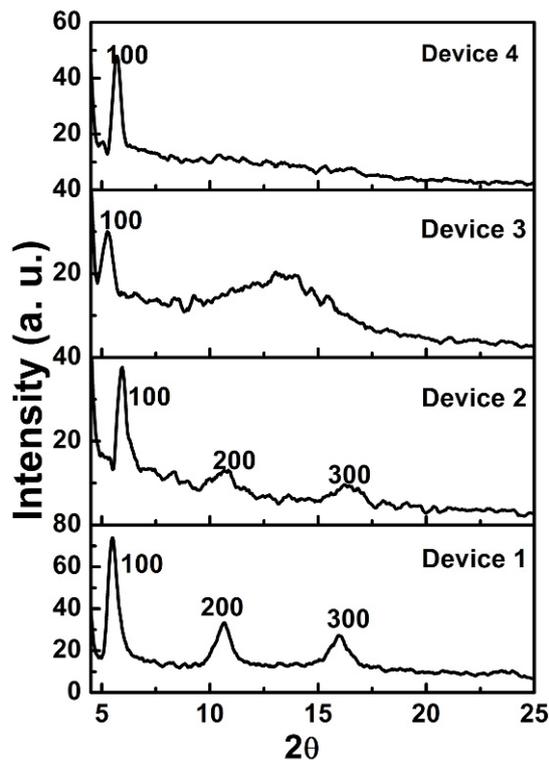


Fig. 3. XRD patterns of the fabricated devices.

in Fig. 1a and Fig. 1b. On the contrary, when the device prepared from dichlorobenzene was subjected to solvent annealing, an increase in current density was observed, as illustrated in Fig. 1c and Fig. 1d. The current flow between source and drain seems to correlate with the degree. The current density is the highest for device 1 and the lowest for device 3. Devices 2 and 4 have almost the same current flow.

It is astonishing to see that solvent annealing improves the charge mobility in the devices made of the films prepared from DCB while it degrades the charge mobility in the devices of the films prepared from CF. We hypothesize that the effect can be attributed to the morphological properties of the film. Pinholes of up to 400 nm in diameter can be observed in the film of device 2 as shown in Fig. 4b. The lower charge mobility in device 2 compared to device 1, both prepared from CF, could be attributed to the nanoporous film induced by SA. This nanoporous morphology can act as transport barrier or transport boundary for the charge carriers within the polymer matrix along the channel de-

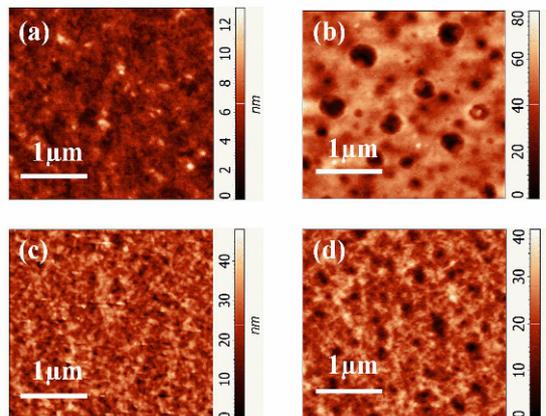


Fig. 4. AFM images of (a) device 1, (b) device 2, (c) device 3, and (d) device 4.

spite the fact that no distinct crystalline domain and grain boundaries were observed. We hypothesize that the early crystallization dominated the overall structure of the film prepared by solvent annealing due to rapid solvent evaporation which led to morphological defects. The film of device 4, as shown in Fig. 3d, indicates the morphology resulting from P3HT aggregation. This aggregation facilitates the stacking interaction between polymer chains and hence improves the molecular order of poorly soluble P3HT prepared from DCB [18]. This is supported by the XRD results for device 4 with higher intensity of (100) peak and the disappearing of (200) and (300) peaks. Since the device 3 and device 4 lacked the long range inter-lamellar order, the solvent annealed DCB induced aggregation within polymer, promoting higher microscopic $\pi - \pi$ stacking order, which is advantageous for charge transport within the polymer domain, hence resulting in improved charge mobility of device 4.

4. Conclusions

In conclusion, we reported comparative study of the OFETs based on RR P3HT polymeric semiconducting films prepared from DCB and CF. The results show that solvent annealing has a significant influence on the OFETs behavior in terms of hysteresis, charge mobility and morphology. Creation

of large nanopinholes effect significantly degrades the OFETs performance.

Acknowledgements

This work was supported by University Malaya Research Grant, Malaysia under research project No RG006/09AFR. We would like to thank Dr James Kingsley from Ossila Limited for useful discussion.

References

- [1] MAJEWSKI L. A., KINGSLEY J. W., BALOCCO C., SONG M., *Appl. Phys. Lett.*, 88 (2006), 222108.
- [2] ZAUMSEIL J., SIRRINGHAUS H., *Chem. Rev.*, 107 (2007), 1296.
- [3] YAN H. et al., *Nature*, 457 (2009), 679.
- [4] LYASHENKO D. A., ZAKHIDOV A. A., POZDIN V. A., MALLIARAS G. G., *Organic Electronics*, 11 (2010), 1507.
- [5] XU W., RHEE S. W., *Organic Electronics*, 11 (2010), 836.
- [6] SIRRINGHAUS H. et al., *Nature*, 401 (1999), 685.
- [7] SETHURAMAN K., OCHIAI S., KOJIMA K., MIZUTANI T., *Appl. Phys. Lett.*, 92 (2008), 183302.
- [8] HUANG J. H. et al., *ACS Applied materials and interfaces*, 1 (12) (2009), 2821.
- [9] KANAI K., MIYAZAKI T., SUZUKI H., INABA, M., OUCHI, Y., SEKI K., *Phys. Chem.*, 12 (2010), 273.
- [10] YANG H., SHIN T. J., YANG L., CHO K., RYU C. Y., BAO Z., *Adv. Funct. Mater.*, 15 (2005), 15 671.
- [11] WANG G., SWENSEN J., MOSES D., HEEGER. A. J., *J. Appl. Phys.*, 93 (10) (2003), 6137.
- [12] KARAKAWA M., CHIKAMATSU M., YOSHIDA Y., OISHI M., AZUMI R., YASE K., *Jpn. J. Appl. Phys.*, 49 (2010), 01AE12-1.
- [13] FU Y., LIN C., TSAI F. Y., *Organic Electronics*, 10 (2009), 883.
- [14] LI G., YAO Y., YANG, H., SHROTRIYA V., YANG G., YANG Y., *Adv. Funct. Mater.*, 17 (2007), 1636.
- [15] FACCHETTI A., *Materials Today*, 10 (3) (2007), 28.
- [16] BRINKMANN M., *Journal of Polymer Science Part B: Polymer Physics*, 49 (2011), 1218.
- [17] MAJEWSKI L. A., SONG A. M., *J. Appl. Phys.*, 102 (2007), 074515
- [18] PARK Y. D., LEE S. G., LEE, H. S., KWAK D., LEE D. H., CHO K., *J. Mater. Chem.*, 21 (2011), 2338.

Received 2012-05-28

Accepted 2012-03-25