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Effects of concentration and annealing on the performance of regioregular poly(3-hexylthiophene) field-effect transistors*

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This paper investigates the effects of concentration on the crystalline structure, the morphology, and the charge carrier mobility of regioregular poly(3-hexylthiophene) (RR-P3HT) field-effect transistors (FETs). The RR-P3HT FETs with RR-P3HT as an active layer with different concentrations of RR-P3HT solution from 0.5 wt% to 2 wt% are prepared. The results indicate that the performance of RR-P3HT FETs improves drastically with the increase of RR-P3HT weight percentages in chloroform solution due to the formation of more microcrystalline lamellae and bigger nanoscale islands. It finds that the field-effect mobility of RR-P3HT FET with 2 wt% can reach 5.78×10^{-3} cm^2/Vs which is higher by a factor of 13 than that with 0.5 wt%. Further, an appropriate thermal annealing is adopted to improve the performance of RR-P3HT FETs. The field-effect mobility of RR-P3HT FETs increases drastically to 0.09 cm^2/Vs by thermal annealing at 150 °C, and the value of on/off current ratio can reach 10^4.

Keywords: field-effect transistors, regioregular poly(3-hexylthiophene) concentration, annealing field-effect mobility

PACC: 8115L, 7360R, 6170A, 7340T

1. Introduction

Organic π-conjugated polymers are regarded as one of the most promising materials for use in 'plastic-electronics' due to their excellent electrical and optical properties.[1] In particular, due to the high field-effect mobility, stability, and solution-processability, regioregular poly(3-hexylthiophene) (RR-P3HT) has drawn much attention as an organic active layer in field-effect transistors (FETs) applying to smart cards, electronic identification tags and active matrix displays.[2−4] Further, the high mobility is attributed to the formation of extended polaron states as a result of local self-organization, in contrast to the variable-range hopping of self-localized polarons found in more disordered polymers.[5] Self-organization in P3HT results in a lamellar structure with two-dimensional conjugated sheets formed by interchain stacking. Sirringhaus *et al*[6] reported that, depending on processing conditions, lamella can adopt two different orientations-parallel and normal to the substrate whose mobilities differ by more than a factor of 100, and can reach values as high as 0.1 cm^2/Vs.[6,7]

Previous work has shown that the microcrystalline lamellar structure formation in RR-P3HT thin films might be a dynamic course during the films growth affected by regioregularity, molecular weight, solvent power, and doping level, etc.[8−11] Obviously, controlling the solution processing conditions of RR-P3HT would directly improve the molecular order of microcrystalline.

However, to the best of our knowledge, present studies on RR-P3HT FETs do not provide sufficient and systemic information about the effects of the or-

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ganic solution's concentrations on morphology, crystallization and charge carrier mobility. Therefore, a systematic study of the crystalline structure and morphology correlations with the charge carrier mobility of RR-P3HT FETs with different concentrations of solution is desired. In this work, we prepare the top-contact (TC) RR-P3HT FETs with different concentrations by using a SiO_2 gate insulator to probe the correlations. Furthermore, we adopt thermal annealing to improve the performance of RR-P3HT FETs, motivated by current reports on improving the crystallinity of the polymeric films through thermal annealing.[12−15]

2. Experimental

The gate insulator layer SiO_2 with 250 nm thickness prepared by electron beam evaporation at deposition rates ($\sim$1 Å$\cdot$s^{-1}) (1 Å = 0.1 nm) on precleaned indium tin oxide (ITO) glass substrates with 25 nm ITO and a sheet resistance of 60 Ohm/sq, and ITO was used as the gate electrode. Then, RR-P3HT thin films were prepared by the spin-coating method (20 μl droplets) with various concentrations (0.5 wt%, 1 wt%, 1.5 wt%, and 2 wt%) in chloroform solution at 2000 rpm for 60 s, and annealed at 90 °C, 150 °C, 240 °C under vacuum atmosphere for about 10 minutes. Subsequently, samples were placed under vacuum for 20 hours to enhance a local self-organization. The thin films average thicknesses of 0.5 wt%, 1 wt%, 1.5 wt%, and 2 wt% are varied about 70 nm, 120 nm, 220 nm and 270 nm, respectively, as measured by a step profilometer (AMBIOS-XP2). RR-P3HT was purchased from Sigma-Aldrich with a greater than 98.5% head-to-tail regiospecific conformation and average molecular weight $M_w \sim$ 64000. Finally, gold (Au) was thermally evaporated through a shadow mask having 150 nm-thick drain and source electrodes. The channel length (L) and width (W) were 25 μm and 1000 μm, respectively. The crystallinity and orientation of RR-P3HT thin films were measured by using x-ray diffraction (XRD, Y-2000). The film surface morphology was investigated by atomic force microscopy (AFM) operated in tapping mode (DI Dimension 3100 manual). The electrical characterization was performed by using a Keithley semiconductor parameter analyzer (Keithley 2612) at room temperature in air.

3. Results and discussion

Figure 1 shows the XRD patterns of RR-P3HT films with various concentrations on a SiO_2 gate dielectric on a ITO glass substrate. The corresponding (100) diffraction peaks to 0.5 wt%, 1 wt%, 1.5 wt%, and 2 wt% are at $2\theta = 5.40$ Å ($d = 16.352$ Å), 5.76 Å ($d = 15.331$ Å), 5.36 Å ($d = 16.474$ Å), and 5.56 Å ($d = 15.882$ Å), respectively. There is a possibility that the molecular axis of P3HT well oriented such that it is parallel to the substrate, and the thiophene rings are perpendicular to the substrate,[9] as shown in inset (b) of figure 1. While inset (a) of figure 1 presents another conformation of the thiophene rings parallelling to the substrate, which results in a lower mobility. Furthermore, we find that the (100) diffraction peak intensity increases gradually with the increase of RR-P3HT concentration, due to the lamellar layer structure enhancement.[11] We confirm that as the concentration increases, it is easier for the RR-P3HT film to form a microcrystalline lamellar structure of preferential orientations of P3HT molecular interchain stacking. Generally, self-organization results in complex microstructures, which has important consequences for electrical properties in FETs.[6]

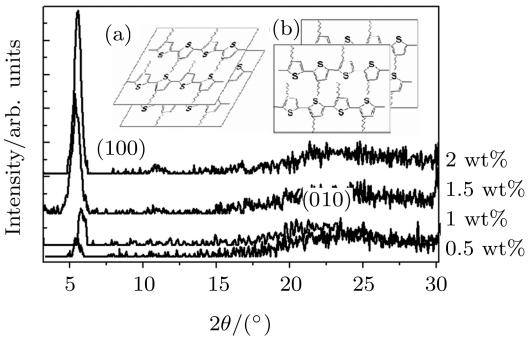


Fig.1. The XRD patterns of RR-P3HT films annealed at 90 °C with various concentrations (0.5 wt%, 1 wt%, 1.5 wt%, and 2 wt%).

Figure 2 shows that noticeable defects and pinholes are not observed for RR-P3HT films with the granular morphologies. The average size of the islands increases for 0.5 wt% (island size of approximately 70 nm), 1 wt% (island size of approximately 100 nm), 1.5 wt% (island size of 100–160 nm), and 2 wt% (island size of 160–200 nm). Further, the average roughness also improves gradually from 0.681 nm, 0.724 nm, 2.496 nm, to 4.718 nm. We find that different concentrations result in distinct differences in

nanoscale islands. It is expected that the size of the nanoscale islands will play an important role in field-effect mobility.[9]

Figure 3 shows that the typical p-type drain current (I_{DS}) versus source-drain voltage (V_{DS}) plots at various gate-source voltages (V_{GS}) for RR-P3HT FETs with different concentrations. The field-effect mobility values of RR-P3HT FETs with different concentrations were calculated in a saturated regime ($V_{DS} = -10$ V) by plotting the square root of the drain current versus gate-source voltage and fitting the data to the equation[16–18]

$$I_{DS} = \frac{\mu W C_i}{2L} (V_{GS} - V_T)^2 .$$

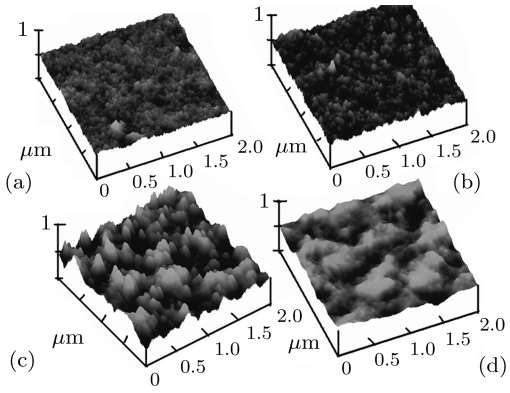


Fig.2. AFM images of RR-P3HT films annealed at 90 °C with various concentrations: (a) 0.5 wt%, (b) 1 wt%, (c) 1.5 wt%, and (d) 2 wt% on a SiO_2 gate dielectric on a ITO glass substrate.

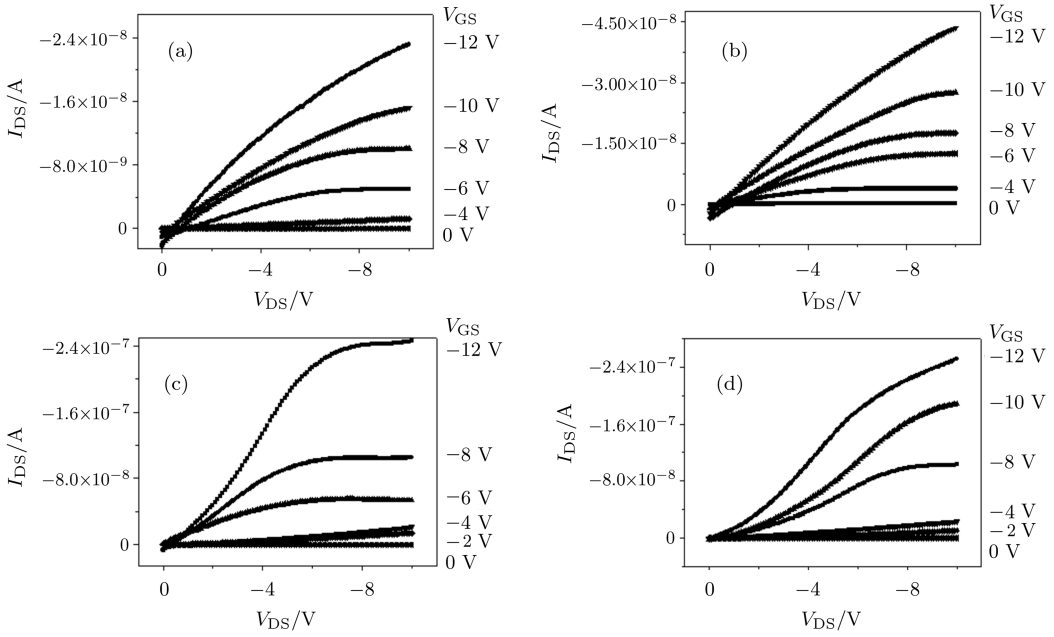


Fig.3. Output characteristics of the RR-P3HT FETs annealed at 90 °C with various concentrations: (a) 0.5 wt%, (b) 1 wt%, (c) 1.5 wt%, and (d) 2 wt%.

Table 1 shows the field-effect mobility and other parameters of RR-P3HT FETs with different concentrations. The field-effect mobility values of RR-P3HT FETs with different concentrations of 0.5 wt%, 1 wt%, 1.5 wt% and 2 wt% were calculated to be 4.39×10^{-4}, 7.8×10^{-4}, 5.37×10^{-3}, and 5.78×10^{-3}, respectively. We find that the field-effect mobility of RR-P3HT FETs increases drastically with the increase of concentration. We also find that the field-effect mobility of RR-P3HT FETs increases drastically with the increase of active layer thickness. The field-effect mobility of FETs with 2 wt% is higher by a factor of 13 than that with 0.5 wt%. Further, the threshold voltage values are at around 0 V, and basically decrease with increasing concentrations. The on/off current ratio values were estimated to be approximately 10^3, and also have a slight increasing trend. The results indicate that RR-P3HT film with a high concentration is easier for forming big nanoscale islands and many microcrystalline lamellae, this fact yields a good performance of the RR-P3HT FETs.

Table 1. The average thickness, the average field-effect mobility (μ), the threshold voltage (V_T), and the on/off current ratio (I_{on}/I_{off}) values at $V_{DS} = -10$ V in saturated regime of RR-P3HT FETs annealed at 90 °C with various concentrations by using 250 nm-thick SiO_2 as gate dielectric layer.

concentrations	average thickness/nm	$\mu/(cm^2/Vs)$	V_T/V	I_{on}/I_{off}
0.5 wt%	about 70	4.39×10^{-4}	1 V	1.25×10^{3}
1 wt%	about 120	7.8×10^{-4}	1.4V	0.5×10^{3}
1.5 wt%	about 220	5.37×10^{-3}	0.66 V	1.67×10^{3}
2 wt%	about 270	5.78×10^{-3}	0.35 V	2.7×10^{3}

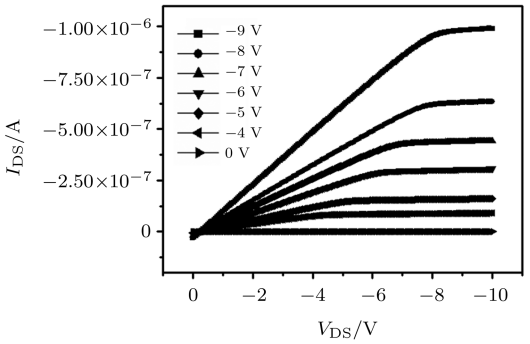


Fig.4. Output characteristics of RR-P3HT FETs with 0.5 wt% annealed at 150 °C for 10 min (subsequently, placed under vacuum for 20 hours).

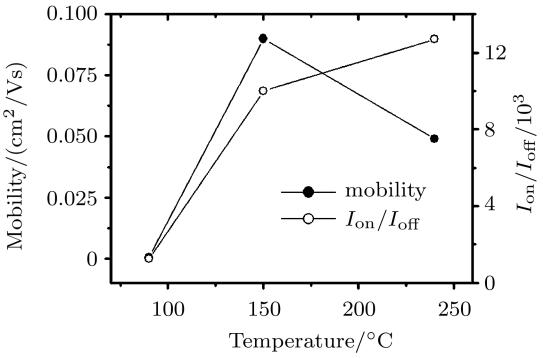


Fig.5. Field-effect mobility and on/off current ratio vs. annealing temperature varied for 90 °C, 150 °C, 240 °C with 10 minutes annealing.

Figure 4 shows the output characteristic curves of RR-P3HT FETs with 0.5 wt% annealed at 150 °C for 10 min, and subsequently placed under vacuum for 20 hours. The field-effect mobility of RR-P3HT FETs increases drastically to 0.09 cm^2/Vs, the field-effect mobility value of the device annealed at 150 °C is higher by a factor of 205 than that annealed at 90 °C. The effect of annealing at different temperatures is also shown in figure 5. The results reveal that the optimum annealing temperature is 150 °C for the field-effect mobility. The on/off current ratio also has an increasing trend from approximately 10^3 to 10^4 with the increase of annealing temperature.

4. Conclusions

In this work, we have investigated the microcrystalline structure and morphology correlations with the charge carrier mobility of RR-P3HT FETs with different concentrations. Due to more microcrystalline lamellae and bigger nanoscale islands of RR-P3HT film with 2 wt%, the field-effect mobility value of RR-P3HT FET can reach 5.78×10^{-3} which is higher by a factor of 13 than that with 0.5 wt%. Further, the field-effect mobility of RR-P3HT FETs increases drastically to 0.09 cm^2/Vs by thermal annealing, and the value of device annealed at 150 °C is higher by a factor of 205 than that annealed at 90 °C. The on/off current ratio also has an increasing trend from approximately 10^3 to 10^4 with the increase of annealing temperature from 90 °C to 240 °C.

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