Charge transport in monolayer poly(3-hexylthiophene) thin-film transistors*

Xu Zong-Xiang(许宗祥)[a)†] and Roy V. A. L.[b)]

[a)] *Department of Chemistry, South University of Science and Technology of China, Shenzhen* 518055, *China*
[b)] *Center Of Superdiamond and Advanced Films (COSDAF), Department of Physics and Materials Science, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong SAR, China*

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It is found that ultrathin poly(3-hexylthiophene) (P3HT) film with a 2.5 nm-thick layer exhibits a higher mobility of 5.0×10^{-2} cm^2/V·s than its bulk counterpart. The crystalline structure of the as-fabricated ultrathin P3HT layer is verified by atomic force microscopy as well as grazing incidence X-ray diffraction. Transient measurements of the as-fabricated transistors reveal the influence of the interface traps on charge transport. These results are explained by the trap energy level distribution at the interface manipulated by layers of polymer film.

Keywords: field-effect transistor, monolayer P3HT, spin coating, grazing incidence X-ray diffraction

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1. Introduction

Organic thin-film transistors (OTFTs) are of immense current interest due to their relatively low cost and potential applications in electronics, including displays, sensors, light-emitting devices, and memory devices.[1–7] To date, many soluble materials have been proposed, but only a few of them can truly possess the high mobilities required for organic circuits. Poly(3-hexylthiophene) (P3HT) is one of the most studied semiconductors for OTFTs. It is solution-processable, commercially available, and exhibits a relatively high charge carrier mobility (>0.1 cm^2/V·s).[8] Intensive research toward improving its mobility has shown that the microstructure in P3HT is critically affected by regioregularity[9,10] and molecular weight,[11] resulting in variation of the field-effect mobilities by several orders of magnitude. Optimization of device preparation, such as dielectric treatment, the deposition method, and choosing an appropriate solvent, has been demonstrated to achieve high mobility.[12–14] In addition, the film thickness of P3HT plays an important role in device performance, and the mobility was found to improve with the increase in film thickness, followed by saturation.[15–18] In the present work, P3HT is spin-coated on a bottom-gate SiO_2/Si transistor substrate, and the transport mechanism in the P3HT monolayer is elucidated. The ultrathin P3HT film (2.5 nm) exhibits a high mobility of 5.0×10^{-2} cm^2/V·s, and the mobility decreases sharply with the increasing film thickness, followed by saturation for film thicknesses higher than 18.8 nm.

2. Experimental details

High-quality head-to-tail coupled regioregular RR-P3HT (regioregularity $>98.5\%$) and other chemicals were purchased from Aldrich. The bottom contact transistors were fabricated and measured according to the method in the literature.[19] The P3HT layer was spin-coated on a patterned SiO_2/Si substrate using P3HT solution in dichlorobenzene, with different concentrations leading to thickness values of of 1 nm, 2.5 nm, 3.2 nm, 4.9 nm, 9.9 nm, 18.8 nm, and 56.5 nm, respectively. The thickness values, surface morphologies, and crystallinities of the deposited layers were measured with an ellipsometer, atomic force microscopy (AFM), and grazing incidence X-ray diffraction (GIXRD),[19] respectively.

3. Results and discussion

Figure 1 shows the output characteristics of field-effect transistors based on P3HT with different thickness values, and the mobility of the P3HT transistors, each as a function of nominal thickness. As depicted in Figs. 1(a)–1(e), each of the devices shows an increase in channel current with the increase in negative gate voltage, which is typical of p-channel transistor behavior with a saturation drain current at high source–drain voltage. Moreover, under the same gate and source–drain voltage bias, the P3HT-based transistor with a thickness of 2.5 nm exhibits the highest channel current of all the transistors. As extracted from the saturation regime of the output curves, a low field-effect mobility of 6.3×10^{-5} cm^2/V·s is observed when the organic film is 1 nm thin. The field-effect mobility increases rapidly to 5.0×10^{-2} cm^2/V·s at a thickness

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†Corresponding author. E-mail: xu.zx@sustc.edu.cn

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of 2.5 nm. A further increase in the thickness of the P3HT film can reduce the mobility of the device, and when the film thickness is beyond 9.9 nm, the mobility reaches a saturation value ($\sim 10^{-3}$ cm^2/V·s). This contradicts the previously reported results of the thickness-dependent carrier mobility in small-molecule OTFTs[20,21] and top-gate architecture P3HT transistors on flexible substrates.[15]

In order to understand the dependence of mobility on film thickness, we analyzed the crystalline structures and morphologies of the as-deposited P3HT films. The crystallinities of the P3HT films with various thickness values, deposited on SiO_2/Si, were examined by GIXRD measurement. As depicted in Fig. 2(a), except for the 1 nm P3HT layer, all the P3HT films, including the ultrathin 2.5 nm layer (the inset in Fig. 2(a)) show a diffraction peak with a 2θ value of 5.3°, which corresponds to the primary (100) peak, indicating that P3HT forms an intraplane structure, with the lamellae oriented along the direction at one degree of order with respect to the direction normal to the substrate, which is inferred from the peak intensity. The intensities for the GIXRD patterns of the as-spin-coated P3HT films at a 2θ value of 5.3° increase linearly with the increasing thickness of the deposited layers, indicating that regular deposition is carried out (Fig. 2(b)). However, no peak shift is observed. This implies that the P3HT in the ultrathin film (2.5 nm) has the same intraplane stacking feature as thicker films. As has been reported previously and from our results, the separation between the P3HT polymer chains is about 1.6 nm and the height of the chain is in a range of about 0.4 Å–0.7Å, which shows that a monolayer of the P3HT polymer is ∼ 2.0 nm thick.[22,23] From these observations, it is obvious that an ultrathin P3HT layer of 1 nm (less than a monolayer) cannot form a network of molecules with enough interplanar stacking, consequently exhibiting a low carrier mobility value.

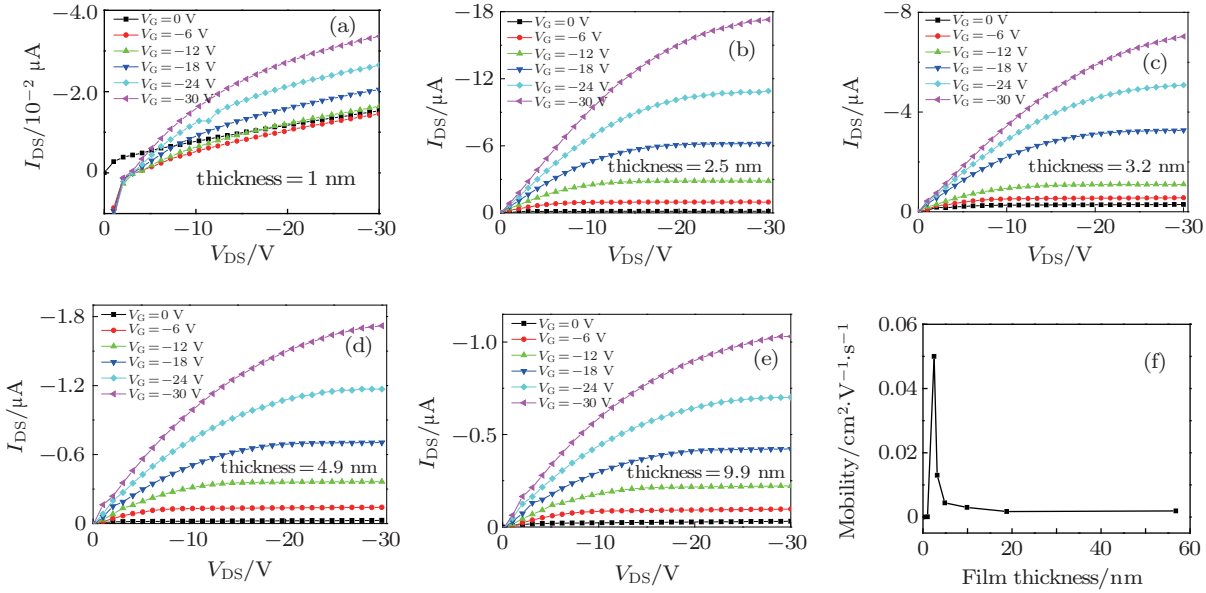


Fig. 1. (color online) (a)–(e) The output characteristics of P3HT-based field-effect transistors with different thickness values, and (f) the charge-carrier mobility versus the thickness of the P3HT semiconductor layer. (Each device has a channel length of 100 μm and a width of 3000 μm.)

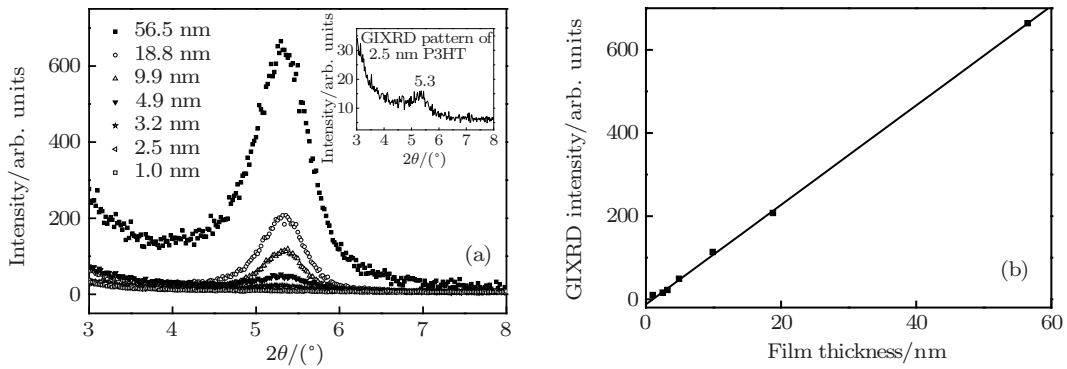


Fig. 2. (a) GIXRD patterns of P3HT spin-coated on SiO_2/Si with various thickness values (inset: the GIXRD pattern of 2.5 nm P3HT), and (b) GIXRD intensity at a 2θ value of 5.3° versus the thickness of the P3HT semiconducting layer.

AFM measurements are carried out to verify the relationship between the mobility and the thin-film morphology. As shown in Fig. 3(a), the ultrathin 2.5 nm P3HT film deposited on SiO_2/Si exhibits a tightly packed grain structure with a grain size of $\sim$10×30 nm, which is favorable for charge transport. However, the thicker P3HT film of 56.5 nm forms a loosely packed fiber network structure with a fiber length of several μm and a width of $\sim$ 10 nm (Fig. 3(b)). In Refs. [24]–[27], it was reported that the planar charge transport and charge mobility of the TFTs are affected by the presence of "interface traps" in the organic semiconductors. To understand the trap states for the thin and thicker films, transient measurements are carried out under ambient conditions.

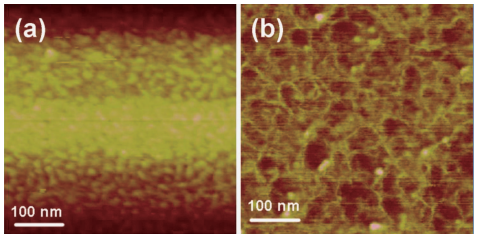


Fig. 3. (color online) AFM images of P3HT spin-coated on SiO_2/Si with thickness values of (a) 2.5 nm and (b) 56.5 nm.

Figure 4 depicts the transient measurements of transistors with P3HT layers of 2.5 nm and 56.5 nm. A constant voltage of −30 V is applied to the gate and −5 V to the drain–source, while the current is measured as a function of time for the 2.5 nm and 56.5 nm P3HT devices. The absolute current decreases much faster for the 2.5 nm thick film P3HT device than for the 56.5 nm thick film. When the gate is biased, the concentration of carriers at the surface would be a δ function, or a function with a steep slope. In a multilayer stacking of molecules like P3HT, the concentration of carriers varies smoothly within a certain distance in the biased condition, and this distance can be the Debye length. Since there are mobile charge carriers flowing from the source to drain, the current density depends on the concentration gradient -grad $(c(x))$. Whenever a concentration gradient of mobile carriers appears, an electrical current is indispensable. The electrical field $(E(x))$, which is caused by the concentration gradient in the multi-stacked layers (x) of the P3HT film, would also induce an electrical field current (drift current) of $j_{\text{field}}(x)$, obeying Ohm's law, which flows in the opposite direction of the electrical diffusion current. At room temperature, we can neglect the diffusion current.[28] Therefore, $j_{\text{field}}(x) = q \times c \times \mu \times E(x)$, with μ = the mobility, and q = the charge of the particle (electron/hole), which is related to the conductivity σ. The total electrical current is mainly dependent on the drift current, and it is well known that the charges flow to the interface when the transistor is biased. In the thick device, due to parallel conduction, the charges cannot affect the interface too much and follow a different distribution of charges in the multilayer film. In addition, the parallel layer on the top changes the thin layer at the interface, or the thick layer on the top changes the structure of the thin layer at the interface. This causes a change in the trap energy level distribution, and eventually affects the conductive states. Therefore, for the 2.5 nm film, the trap at the interface plays a more important role than the bulk film, and this can be seen from the fast trapping of charges (fast decay of channel current) for the 2.5 nm thick film.

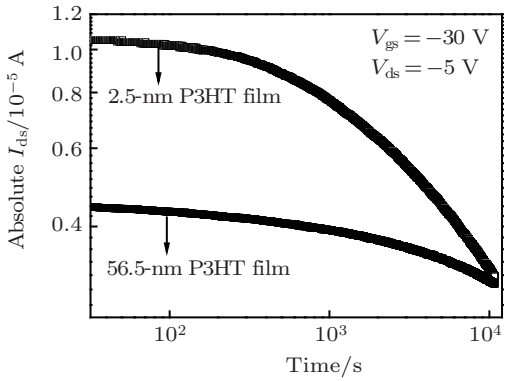


Fig. 4. Transient measurements of transistors with 2.5 nm and 56.5 nm P3HT layers (devices with a channel length of 100 μm and width of 3000 μm).

4. Summary

In this work, we fabricated P3HT-based transistors with various thicknesses by spin coating on an SiO_2/Si substrate. The devices each show a thickness-dependent transport property. The ultrathin monolayer of 2.5 nm thick P3HT exhibits a highest charge carrier mobility of 5.0×10^{-2} cm^2/V·s. Increasing the film thickness leads to a decrease followed by a saturation of a mobility of $\sim10^{-3}$ cm^2/V·s. GIXRD and AFM measurements reveal the crystalline grain structure of the P3HT monolayer, and transient measurements of as-fabricated transistors show the influence of the interface on charge transport. We attribute these results to the trap energy level distribution at the interface, which has been manipulated by the parallel layers of the polymer for the bulk film.

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