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Letter

Field-effect transistor characteristics and microstructure of regioregular poly(3-hexylthiophene) on alkylsilane self-assembled monolayers prepared by microcontact printing

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ABSTRACT

Molecular orientation of regioregular poly(3-hexylthiopene) (P3HT) on self-assembled monolayers (SAMs) of octadecyltrichlorosilane (OTS) prepared by microcontact printing (μCP) are investigated using grazing-incidence X-ray diffraction and field-effect measurements. Spin-coated P3HT films on OTS SAMs fabricated by the μCP method are less oriented and exhibit lower diffraction intensity than those prepared by conventional liquid phase deposition (LPD). In spite of the lower crystallinity, the field-effect mobility in P3HT film on μCP-OTS is almost the same as that on LPD-OTS. This result is attributed to the lower density of trapping centers in P3HT films on μCP-OTS, which is manifested by the lower subthreshold swing of transistor characteristics of P3HT films on μCP-OTS.

1. Introduction

Organic field-effect transistors (OFETs) have drawn much attention as a key technology for realizing lightweight, large-area, low-cost, and flexible electronics such as active-matrix light-emitting displays, electronic papers, and radio frequency identification tags [1–4]. Soluble organic semiconductors have attracted increasing interest because of their compatibility with printing processes, and regioregular poly(3-hexylthiophene) (P3HT) is a promising candidate because of its high charge mobility. The electrical characteristics of P3HT films have been reported to depend on the regioregularity [5], the molecular weight [6,7], the casting solvent [8], and the surface properties of gate dielectrics [9,10].

The surface treatment of gate dielectrics with hydrophobic self-assembled monolayers (SAMs) such as hexamethyldisilazane and octadecyltrichrolosilane (OTS) has been found to induce the crystallization and orientation of P3HT polymers, which leads to an increase of several orders-of-magnitude in the field-effect mobility [5,9,10], and SAM treatment is crucially important for improving OFET performance. For the deposition of SAMs, liquid phase deposition (LPD) has been commonly used. An alternative approach consisting of microcontact printing (μCP) [11,12] has been extensively studied for microelectronic and biological applications because of its technological advantages. The μCP method allows the direct printing of SAMs and high-throughput production of OFET arrays on large-area substrates has been demonstrated using selective deposition of soluble semiconductors on μCP-SAMs [13,14]. However, the microstructures of organic semiconductors on μCP-SAMs and their electrical characteristics have not been fully investigated.

In this letter, we use grazing-incidence X-ray diffraction (GIXD) and FET measurements to investigate the microstructure and electrical characteristics of P3HT films on OTS SAMs prepared by the μCP and LPD methods. P3HT

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on μCP-OTS is less ordered and exhibits a lower crystallinity compared with P3HT deposited on conventional LPD-OTS. In spite of the lower degree of crystallinity, P3HT FETs fabricated on μCP-OTS exhibit a high field-effect mobility that is comparable to the mobility for LPD-OTS. Furthermore, P3HT FETs on μCP-OTS exhibit even better subthreshold characteristics.

2. Experimental section

A highly doped Si wafer with a 300-nm surface layer of thermally grown SiO_2 was used as a substrate. The substrate was immersed in hot, concentrated H_2SO_4 for 30 min and then repeatedly washed with deionized water, acetone, and hexane in an ultrasonic bath, followed by UV/O_3 cleaning. For the μCP, a poly(dimethylsiloxane) (PDMS) sheet was used as a stamp. The PDMS stamp was immersed in a solution of 50 mM OTS in hexane for 1 h. After removing it from the solution, the PDMS stamp was dried for 10 min and put in contact with the SiO_2 substrate surface for 2 h to fabricate the OTS SAM. The OTS-modified substrate was then rinsed with hexane and ultrasonically cleaned in ethanol for 1 min to remove any excess layers. Finally, the substrate was dried at 100 °C for 5 min. For the LPD, the cleaned Si/SiO_2 substrate was directly immersed in a solution of 10 mM OTS in anhydrous toluene for 7 days, and then rinsed with toluene and ultrasonically cleaned in ethanol for 1 min. Other treatments were the same as those for the μCP-SAMs. All SAM depositions were performed under an N_2 atmosphere with a humidity of approximately 3%. The formation of SAMs on the substrate was confirmed by ellipsometry and water-contact angle measurements. Plexcore OS 1100 P3HT (regioregularity > 95%, average molecular weight = 25,000–35,000, Plextronics, Inc.) was used. P3HT thin films were fabricated onto the OTS-treated substrates by spin coating from 1 wt.% solution in toluene under ambient conditions. The thicknesses of P3HT films were approximately 100 nm on both μCP and LPD SAMs. GIXD measurements were performed at the beam line BL46XU of the SPring-8 synchrotron at the energy of 10 keV. Rocking curves were measured in the secular setup looking at the (1 0 0) peak by Cu Kα X-rays (~8.0 keV) with a rotating target energy of 15 kW.

For FET measurements, gold source and drain electrodes were evaporated onto the P3HT films through a shadow mask. The channel length and width were 50 μm and 1.5 mm, respectively. The FET characteristics of the fabricated devices were measured in ambient conditions after annealing at 150 °C under vacuum for 1 h.

3. Results and discussion

We carefully deposited the SAMs under controlled water conditions to obtain good SAMs with smoother surfaces [15]. Table 1 shows the characteristics of OTS SAMs prepared by the μCP and LPD methods on SiO_2 surfaces. Ellipsometry measurements indicate that both OTS SAMs are slightly thicker than reported values of about 28 Å [16,17]. However, the thicknesses are constant for prolonged deposition of OTS, indicating the formation of well-defined monolayers. Both OTS-treated surfaces have a high water-contact angle and a small root mean square (R_{MS}) roughness, which are comparable to published values [16,17]. No clear differences between both SAMs were observed by these measurements.

Table 1
Ellipsometric thickness, water-contact angle, and RMS roughness of OTS SAMs prepared by μCP and LPD methods.

	Thickness (Å)	Contact angle (°)	R_{MS} (Å)
μCP	30.8	108	4.7
LPD	29.3	108	5.7

Fig. 1(a) and (b) shows the typical transfer characteristics of P3HT FETs on OTS SAMs fabricated by the μCP and LPD methods, respectively. Both devices exhibit good FET characteristics with on/off ratios of over 10^3, but the device with μCP-OTS exhibits a lower subthreshold swing than that with LPD-OTS. The electrical performance of P3HT FETs is summarized in Table 2. We characterized more than 40 devices for each OTS SAM. The field-effect mobilities of the devices on each OTS SAM are almost the same, and are typical of P3HT with similar molecular weight [9,10]. However, the device on μCP-OTS has a smaller negative threshold voltage V_{th} compared with LPD-OTS. Similar negative V_{th} has generally been observed in P3HT FETs with OTS-treated substrates [5,9]. The smaller V_{th} in the device on μCP-OTS indicates a lower density of charge traps at the P3HT/SiO_2 interface [18], which leads to good subthreshold characteristics, as shown in Fig. 1(a).

Fig. 2(a) and (b) shows the out-of-plane and in-plane GIXD patterns of P3HT films spin-coated onto LPD-OTS and μCP-OTS SAMs, respectively. For the P3HT film on LPD-OTS, three orders of intense peaks are observed in the out-of-plane pattern, and the in-plane diffraction displays a distinct (0 1 0) peak. The (h 0 0) and (0 k 0) diffraction peaks of P3HT films are attributed respectively to a lamellar structure caused by interdigitating alkyl side chains and π-stacked polymer backbones that result from the self-organization of P3HT molecules [5].

The results for the P3HT film on LPD-OTS indicate that highly ordered lamellae are preferentially oriented parallel to the substrate (edge-on orientation). Such self-orientation behavior on SAM-treated substrates is consistent with previous reports [5,9,10] and provides efficient π-stacking of P3HT molecules along the substrate surface and enhanced field-effect mobility. In contrast, P3HT orientation on the μCP-OTS is quite different. The out-of-plane diffraction of the P3HT film on the μCP-OTS shows relatively intense (1 0 0), (2 0 0), and (3 0 0) peaks and, in addition, exhibits a clear (0 1 0) peak. For in-plane diffraction, the (0 1 0) peak disappears. This result indicates that μCP-OTS induces face-on orientation of P3HT molecules and decreases π–π stacking along the in-plane direction.

The rocking-curve measurement also reveals the decrease in edge-on oriented structure for P3HT film on the μCP-OTS surface (Fig. 3). The intensity of the (1 0 0) lamella peak for P3HT film on μCP-OTS is weaker than that for P3HT film on LPD-OTS. However, the peak width for P3HT film on μCP-OTS is almost the same as that for