고분자 기판 상에 Rubber-stamp-printing 방법으로 제작한 유기박막 트랜지스터에 관한 연구

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Rubber-stamp-printed Poly (3-hexylthiophene) organic field-effect transistor on a plastic substrate with high mobility

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Abstract

We report high performance poly (3-hexylthiophene) organic field-effect transistors fabricated on a plastic substrate. The polymer active channel layer was directly printed by the rubber stamp printing method with a pre-patterned elastomer stamp. As a result, organic transistors having average field-effect mobility of 0.079 cm^2/Vs and on/off ratio of 10^4 ~ 10^5 were realized on a plastic substrate. Also, through the investigation of the molecular ordering of rubber-stamp-printed poly (3-hexylthiophene) films using synchrotron grazing-incidence X-ray diffraction measurements, the films were found to have edge-on structure which is favorable in realizing high performance organic transistors.

Key Words : OTFT, rubber-stamp-printing, plastic substrate, poly (3-hexylthiophene)

1. 서 론

Polymer semiconductors are very promising materials for future organic based electronics such as flexible displays, electronic papers, photovoltaic devices and integrated circuits[1,2]. The most important reason of using polymer is that polymer films can be easily obtained using low-cost processes such as spin-coating, ink-jet printing and rubber stamp printing. Particularly, the rubber stamp printing has received considerable attention lately because this technique does not require any photolithographic process during the device fabrication and direct printing of various films are possible. Recently, metal lamination technique using a rubber stamp has been reported by Loo et al.[3] which enables direct printing of metal thin films on a plastic substrate. In this approach, with combination of polymer film printing technique, all-printed electronics will be possible on various kinds of substrates.

In this report, we demonstrate organic field-effect transistors (OFETs) fabricated using the rubber stamp printing method. The poly (3-hexylthiophene) (P3HT) active channel layer was printed with a pre-patterned rubber stamp eliminating any photolithographic process required for patterning the polymer layer.

Also, it is expected that printed polymer films have different molecular ordering structure compared to spin coated films due to the unique film formation mechanism in rubber stamp printing. To analyze and compare the molecular ordering of the spin coated and printed polymer films, synchrotron grazing-incidence X-ray diffraction (GI-XRD) measurements were carried out.

2. 실험

Figure 1 shows the schematic diagram of a bottom-contact type OFET device. The gate electrode, Al or Ni, was deposited by rf-magnetron sputtering system on a 192 ㎛-thick polycarbonate substrate at room temperature. The thickness of the gate electrode was 100 nm. The gate insulator has been made of 250 nm-thick SiO_2 deposited by e-beam evaporator at 110°C. The source and drain electrodes which consist of Cr (20 nm) and Au (70 nm), were deposited sequentially by e-beam evaporator and thermal evaporator. The channel length (L) and width (W) were 25 and 500 ㎛, respectively. After patterning the source and drain electrodes, O_2 plasma and hexamethyldisilazane (HMDS) treatments were followed sequentially to modify the surface property of the gate insulator[4].

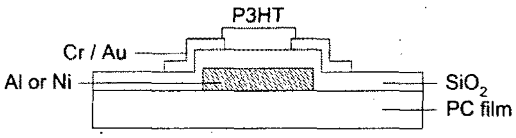

Fig. 1. Schematic diagram of bottom-contact type organic field-effect transistor (OFET).

The annealing conditions such as temperature, atmosphere and annealing time have significant effects on the electrical characteristics of the device[5]. Here, the devices were annealed at 90°C for 2 hours in a vacuum oven. The electrical properties were measured with Keithley 4200-SCS semiconductor characterization system and GI-XRD measurements were performed using the 8C1 beamline at the Pohang Accelerator Laboratory (PAL) to investigate two-dimensional molecular ordering P3HT films.

3. 결과 및 고찰

In order to increase the regioregularity of P3HT material, a purification process of continuous extraction with tetrahydrofuran (THF) and acetonitrile was carried out, using solubility difference between regio-random and regioregular polymers. The regioregularity of the sample has been increased from 93% to 98% after the purification process which is estimated with ^1H NMR by comparing the signal intensity that arises from the aromatic region of the spectrum[6].

Purified P3HT was then dissolved in chloroform with concentration of 0.2 wt% and printed by rubber stamp printing method in following steps. At first, to create the rubber stamp, a master structure with 10 x 10 rectangular type islands was fabricated on a Si wafer using SU-8 photo-resist (MicroChem corp.). The thickness of the photo-resist was 400 ㎛. Later, poly (dimethylsiloxane) (PDMS) (DC 184, Dow Chemical) prepolymer was poured on the master structure and cured at 60°C for 12 hours in an oven. After the curing process, the rubber stamp was removed from the master structure. Then, a drop of P3HT solution was supplied on the rubber stamp and blown with a stream of nitrogen, leaving a thin film of polymer on the stamp. Finally, the stamp was contacted directly with the substrate to transfer the film onto the substrate forming the active channel.

Figure 2 shows the optical images of fabricated PDMS rubber stamp and printed P3HT film on a polycarbonate substrate. The size of the island pattern is 700 ㎛ x 900 ㎛ and the thickness of the film is 60 nm. The thickness uniformity of the P3HT films was near 80% in 100 island patterns.

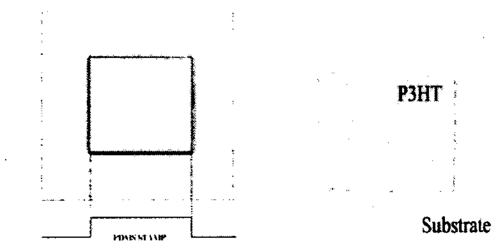

Fig. 2. Optical images of (a) rubber stamp, (b) rubber-stamp-printed P3HT film on a plastic substrate (700 ㎛ x 900 ㎛).

The relationship between the microstructure of P3HT films and the electrical characteristics of field-effect transistor has been intensively studied since after the first investigation by Sirringhaus et al.[7]. This report showed that, the field-effect mobility of organic transistor depends on the two-dimensional molecular ordering of P3HT film and the edge-on structure is more favorable in achieving high mobility rather than the face-on structure.

In order to investigate the structural properties of rubber-stamp-printed P3HT films, synchrotron GI-XRD measurements were carried out on both spin coated and rubber-stamp-printed P3HT films on Si/SiO_2 substrates. Here, purified P3HT material with 98% in regioregularity has been used and the molecular structure of P3HT is shown in Fig. 3.

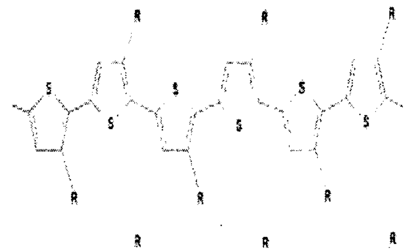

Fig.3. Molecular structure of P3HT.

To minimize the scattering contributions from the substrate during the synchrotron measurements, the grazing incidence angle was fixed at 0.18° which is between the critical incidence angles of SiO_2 (0.20°) and polymers (0.17°). Fig. 4 shows diffraction patterns obtained from the samples in out-of-plane mode. The first peak (2Θ=5.5°) corresponds to (100) and the second (2Θ =11°), third (2Θ=16°), fourth (2Θ=24°) peaks represent (200), (300), (010), respectively[6,8]. The (100), (200) and (300) reflections correspond to the lamellar type stacking of the two-dimensional conjugated planes (d = 16.7 Å) and (010) reflections correspond to the π-π interchain stacking distance between the polymer chains (d = 3.8 Å).

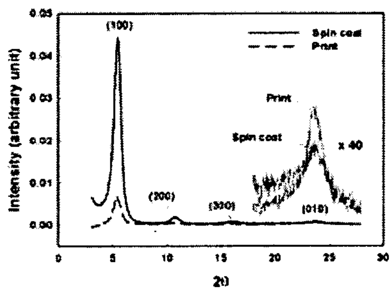

Fig. 4. Diffraction patterns of spin coated and rubber-stamp-printed P3HT films.

Results show that strong (100) reflections were observed in spin-coated as well as printed P3HT films, whereas (010) reflections were very weak. This implies that the (100)-axis has the preferred orientation normal to the film surface.

The difference in the intensity of (h00) (h = 1, 2, 3) reflections in spin coated and printed films may result from the difference in film thickness. However, the intensity of (010) reflections in printed film is higher than spin coated sample, suggesting that printed films have more random structure than spin-coated films. This is due to the different film forming conditions during the rubber stamp printing process. In rubber stamp printing, P3HT film is formed with a very rapid growth rate by a stream of N_2 gas and consequently results in more disordered structure than spin coated films. However, despite the fact that the printed films have less ordered structure than spin coated films, it has preferential orientation of (100)-axis normal to the film surface and suggests that the organic transistors with high field-effect mobility can be achieved using the rubber stamp printing.

Figure 5(a) and 5(b) show the transfer characteristics of organic transistors fabricated with as-received (93% in regioregularity) and purified (98% in regioregularity) P3HT materials. Here, the active channel was printed using the rubber stamp. With low regioregular material (93%), the field-effect mobility was found to be 0.025 cm^2/Vs and the on/off ratio was $10^2 \sim 10^3$ (Fig. 5(a)). However with purified material (98%), the field-effect mobility increased to 0.079 cm^2/Vs with a maximum value of 0.1 cm^2/Vs and the on/off ratio also increased to $10^4 \sim 10^5$ (Fig. 5(b)). Consequently, using higher regioregular P3HT, field-effect mobility and on/off ratio were improved by factors of 3 and 102, respectively.

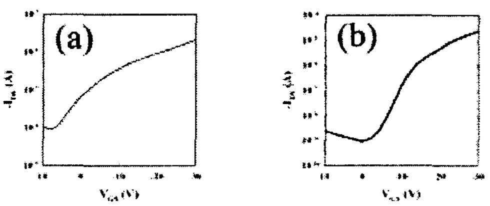

Fig.5. Transfer characteristics of rubber stamp printed OFETs on polycarbonate substrates with (a) as-received P3HT (93% in HT regioregularity), and (b) purified P3HT (98% in HT regioregularity). (L= 25μm, W=500μm, V_{DS} = -30V).

4. 결 론

In summary, organic transistors having high field-effect mobility and on/off ratio were realized on a plastic substrate using the rubber stamp printing method. Through the investigation of the molecular ordering of rubber-stamp-printed P3HT films, the printed films showed preferential orientation of (100)-axis normal to the film surface or edge-on structure providing high field-effect mobility.

감사의 글

This work was supported by grant No. RTI04-01-02from the Regional Technology Innovation Program of the Ministry of Commerce, Industry and Energy (MOCIE).

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