

## Device Characteristics of FETs Made From a p-doped Polythiophene Solution

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### 1. Introduction

Regioregular, head-to-tail poly(3-*n*-hexylthiophene) (HT-P3HT) has been intensively studied to gain a deep insight into the charge carrier transport in field-effect transistors (FETs) since several research groups succeeded in observing high hole mobility ( $\mu_{fet}$ ) of more than  $10^{-1}$  cm<sup>2</sup>/Vs [1], [2]. It has been intuitively explained that, in these FETs, the hole transport efficiency is improved by hole conduction through ordered domains densely formed in the active layer, and has been believed that the higher regioregularity of the polymer act effectively for self-organization of the ordered structure in the film formation from solution. By contrast, one or two order lower  $\mu_{fet}$  have been often reported for the similar FETs used in the sensational studies, suggesting that the origin of the efficient hole transport can not be completely ascribed to the thin-film morphology organized by the molecular stereoregularity [3]. In this paper, we report that device performance such as  $\mu_{fet}$  and on/off ratio can be markedly improved in the FET, where the active layer was prepared from a p-doped solution of HT-P3HT. While the solution doping enhanced the interchain face-to-face interaction in the ordered structure, the dependence of the device characteristics on the doping level indicated that initial hole concentration in the active layer have the major contribution to the improvement in the FET performance.

### 2. Experiments

Fig. 1 shows the chemical structure of HT-P3HT and device structure of the FETs investigated in this study. Commercial HT-P3HT was purified and fractionated by means of GPC, and a polymer sample with an  $M_w$  of ~37000,  $M_w/M_n$  of ~1.4, and regioregularity of more than 98 % was used in this study.

The FETs were fabricated on an n<sup>++</sup>-Si wafer with a 200 nm-thick SiO<sub>2</sub> layer, which functioned as a gate electrode and a gate insulator, respectively. The SiO<sub>2</sub> surface was modified with hexamethyldisilazane by immersing in a 20 vol % solution prior to active layer fabrication. Au was used for the source and drain electrodes, which were vacuum-evaporated on top of the active layer through a metal shadow mask. The channel width and channel length determined by the electrodes were 500  $\mu$ m and 20  $\mu$ m, respectively. The HT-P3HT layer was spin-coated from a 0.1 wt % CHCl<sub>3</sub> solution. NOBF<sub>4</sub> (as a CH<sub>3</sub>CN solution) was used for the p-doping of the polymer molecules in the solutions. The thin films were also prepared on an SiO<sub>2</sub> substrate to compare the thin-film structure by optical ab-

sorption spectroscopy. Device characteristics of the FETs were measured in N<sub>2</sub> atmosphere according to the previously reported method [3].

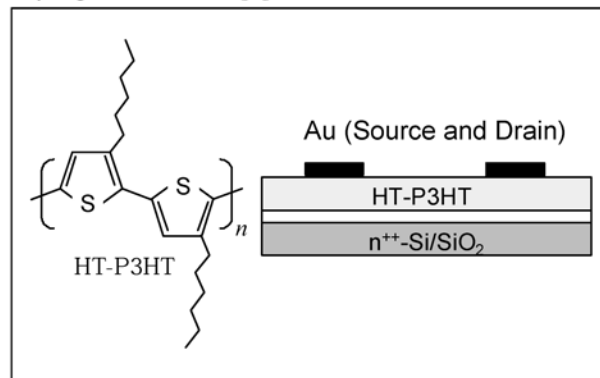


Fig.1. Chemical structure of HT-P3HT and device structure of the FET used in this study.

### 3. Results and Discussion

Fig. 2 shows the optical absorption spectra of the spin-coated HT-P3HT films prepared from the non-doped and doped solutions. The thin films exhibited a vibronic feature peaking around 520, 550 and 610 nm for the main-chain photoabsorption as has been observed for the solid films of this kind of polymers. For the films obtained from the p-doped solutions, a broad absorption was observed in the near-infrared region. The low-energy absorption has been attributed to an electronic transition process of positively charged species, which have holes stabilized on the conjugated main chain with a quinoid form (namely, polaron and/or bipolaron).

We found that the relative intensity of ~610 nm peak increased with the increase in the NOBF<sub>4</sub> concentration in the solution. We confirmed that the increase was not responsible for overlapping of the near-infrared absorption onset; in contrast to breaching of the near-infrared absorption, the vibronic feature exhibited negligible change after the thin films were electronically reduced by exposing hydrazine vapor. It has been proposed that the optical absorption around 610 nm correlates with the magnitude of the face-to-face intermolecular electronic interaction of the  $\pi$ -stacking of the polythiophene main chain [4]. The increase in the relative absorption intensity, therefore, suggests that the ordering of the interchain  $\pi$ -stacking can be improved with the increase in the oxidation level of HT-P3HT in solution. We estimate that planarity of the polymer main chain was raised by the quinoid structure

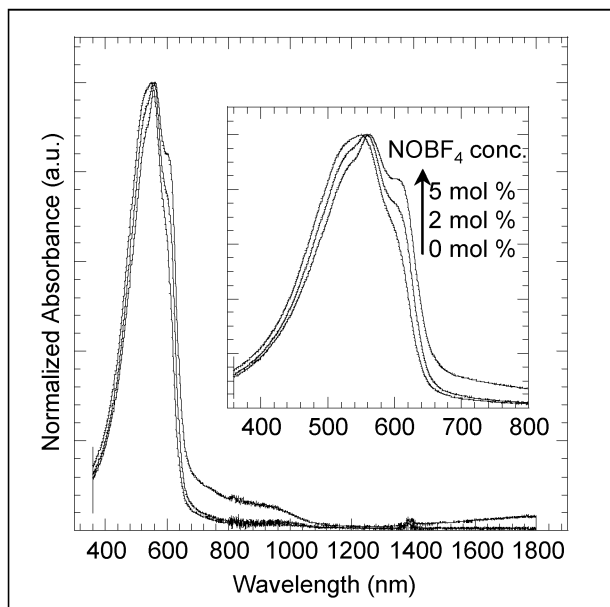


Fig. 2. Absorption spectra of the spin-coated thin films from the non-doped and doped (2 and 5 mol %) HT-P3HT solutions. The inset shows the absorption spectra in the visible region.

partly generated in the oxidized polymer molecules in the solution. The development of the rigid, planar conformation likely enhances the face-to-face packing among polymer chains and thus promotes the organization of the ordered structure.

Device characteristics of the FETs were, however, affected significantly by the electronic property of the active layer rather than the difference in the thin-film structure caused by the solution doping. Fig. 3 shows the dependence of the transfer characteristics on the  $\text{NOBF}_4$  concentration of the solution. The much higher off current than that of the non-doped FET is generally explained by an increase in the off-state conductivity of the active layer, where the initial hole concentration was raised due to the oxidative doping of HT-P3HT in the solution for the 2 and 7.5 mol %-doped thin films.

By contrast, the FET with the 5 mol %-doped thin film showed a different behavior from that predicted from the other FETs with the doped active layer. As shown in Fig. 3, The 5 mol % doped FET exhibited much better on/off performance together with markedly improved  $\mu_{\text{fet}}$  (from  $2.0 \times 10^{-3}$  to  $3.2 \times 10^{-2} \text{ cm}^2/\text{Vs}$ ) compared with the non-doped active layer. We observed that the  $\mu_{\text{fet}}$  dropped to  $2.0 \times 10^{-2} \text{ cm}^2/\text{Vs}$  when the active layer was reduced by the hydrazine vapor exposure, which have negligible influence on the thin-film structure as described above. These results indicate that the device characteristics including the carrier transport property is dominated chiefly by the initial hole concentration of the active layer rather than the thin-film structure of the active layer in the HT-P3HT-based FETs. Taking account of the fact that improved  $\mu_{\text{fet}}$  ( $2.0 \times 10^{-2} \text{ cm}^2/\text{Vs}$ ) was also observed for the 2 mol % doped active layer, there must be an appropriate range of the initial hole concentration that satisfy the efficient carrier transport and

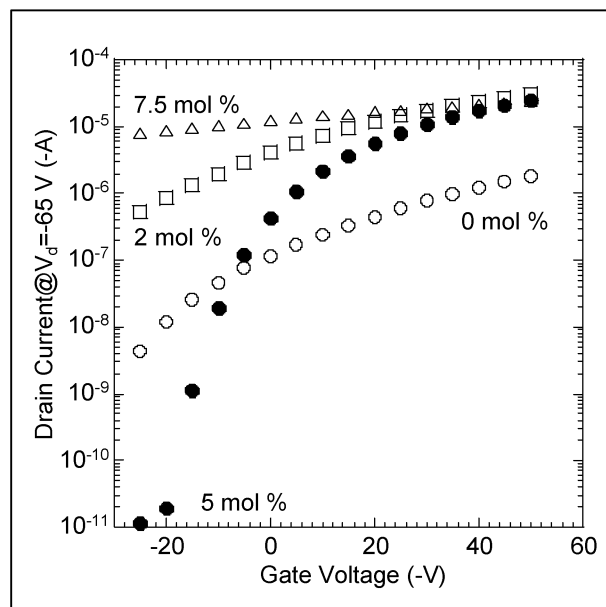


Fig. 3. Dependence of the transfer characteristics of the FETs on the  $\text{NOBF}_4$  concentration in the HT-P3HT solution.

field-effect modulation.

#### 4. Conclusion

By using the appropriately p-doped solution, we succeeded in raising the device performance of the HT-P3HT-based FETs. We concluded that the hole concentration of the active layer is one of the important factors in obtaining the  $\mu_{\text{fet}}$  from the FETs. We estimate that the large difference in the  $\mu_{\text{fet}}$  reported for the this class of FETs is, to a certain extent, due to the use of polymer samples in various doping levels, which possibly depend on sample purity.

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