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# Electrical characterization of a P3HT thin film prepared by an applying-field casting method

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The controllability of field effect transistor (FET) characteristics was investigated for polymer FET prepared by an applying-field casting method. Solution of a poly(3-hexylthiophene) (P3HT) used as an active layer of FET was cast on the substrate with source and drain electrodes. Electric field was applied between the two electrodes during the film formation. Reference samples showed a characteristic of normally-off type, field-applied samples showed a characteristic of normally-on type. The electric field dependence and the channel length dependence were also investigated, which may lead to the fabrication of the devices having desired functions. Current between the electrodes was measured during the film formation by the applying-field casting method. X-ray diffraction (XRD) pattern concerning the molecular ordering showed that the long chain was parallel to the substrate. Current data show the phenomenon closely related to the formation of a molecularly ordered conducting pass.
Key words: P3HT, organic FET, field applied casting, polymer

## 1. INTRODUCTION

Organic semiconductive materials, especially polymers, are greatly attracted as flexible electronic components [1, 2]. Solution process including casting, dipping, spin-coating or printing technologies are found to be suitable for the fabrication of polymer thin films, because of the low cost and large area preparation of the devices compared to the vacuum processes. All-polymer inverter circuits for an integrated circuit (IC) using solution process is already reported [1, 3]. More complicated integrated circuit consisting of multiple inverter circuits demands a level-shift resistance since all complementary circuits have a voltage shift between input and output. With a threshold voltage controllable FET, such a voltage shift resistance is not needed. This indicates that a high performance and controllability of the characteristics can be expected for organic FETs.

An applying-field casting method, proposed here, is a novel and useful technique to control the FET characteristics. Electric field is applied to the channel region to control the molecular arrangement during the film formation. The applying field effects on the film growth are reported for TTF-TCNQ [4] and CNT [5]. Electrical stimulation can affect the molecular ordering and a novel characteristic is expected. An applying-field casting method is done without any special equipment and can be applied to other wet processes such as ink jet printing [3]. In this paper we report the controllability of FET characteristics by applying-field casting method, their dependences on electric field strength and channel length. The probability of fabrication of components with arbitrary function using this method will also be discussed.

## 2. EXPERIMENTAL

Figure 1(a) shows the chemical structure of P3HT. Reioregular P3HT should be an exceptionally promising candidate to realize all-organic circuits by low-cost processes with their high performance and easy processability [6, 7]. Its well-defined molecular architecture is as in Fig. 1(b) results in well-ordered structure and high mobility.

Figure 2 shows the schematic drawing of the polymer FET fabricated by applying-field casting method. Two sets of Au source and drain electrodes were deposited through a shadow mask onto the Si substrates with 300 nm $SiO_2$ gate oxide (thermal oxidation: 1100℃, 3 h). P3HT was cast on the substrates with the electric field between one pair of source and drain electrode for 60 min in nitrogen atmosphere saturated with chloroform vapor. On the other hand, the other pair of source and drain electrodes is the reference sample. To examine the effect of the applying-field casting method, we measured the FET characteristics of the two samples having equivalent P3HT film thickness. The electric-field-strength dependence and the channel

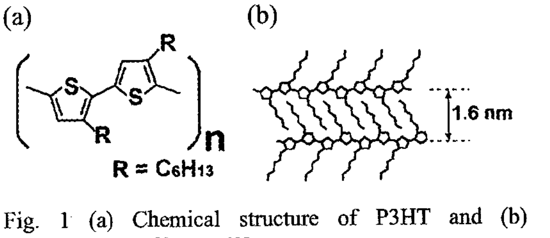


Fig. 1 (a) Chemical structure of P3HT and (b) superstructure of P3HT [8].

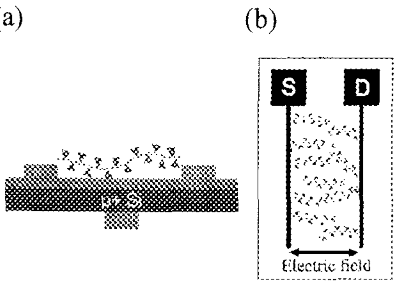


Fig. 2 Sectional view and top view of the organic FET fabricated by applying-field casting method.

length dependence were also investigated, varying the channel length ($L$) as 20, 50, 100 μm with a channel width ($W$) of 5 mm.

XRD measurements require larger active area than that of the present FET sample. Large size interdigital electrodes were, therefore, adopted for the XRD measurements, where $L$ = 100 μm and $W$ = 120 mm. The applied-field sample and the reference sample were fabricated on different substrate in this case also. The two samples were, however, simultaneously fabricated under the equivalent condition.

Regioregular P3HT and high purity grade solvents were purchased from Aldrich Chemical Co. and Wako Pure Chemicals Industries, Ltd., respectively. Regioregular P3HT was purified, reducing the impurity content with EDTA prior to the film deposition. Chloroform solution of P3HT with the concentration of 0.1wt% was used. All solutions were filtered through a 0.20 μm pore size PTFE membrane syringe filter. All samples were fabricated in nitrogen atmosphere saturated with chloroform vapor at room temperature. The electrical characteristics of these samples were measured in vacuum. The current-voltage ($I$-$V$) characteristics were measured with a Hewlett-Packard 4041B picoammeter/voltage-source.

## 3. RESULTS AND DISCUSSION

Typical current-voltage characteristics of P3HT top-contact FET are shown in Fig. 3(a). Field effect mobility and on-off ratio were approximately 7.5x10$^{-3}$ cm$^2$/Vs and 10$^7$, respectively. Figure 3(b) shows the $I$-$V$ characteristics of the P3HT bottom-contact FET, whose currents are lower than those of top-contact FET due to the difference of their crystallinity and contact resistance between the electrode and the active layer. Figure 4 shows the current voltage characteristics of P3HT-FET of the field-applied sample and the reference sample when the applied electric field strength is 5 kV/cm (20 μm, 10 V). Mobilities of the reference sample and the field-applied sample are 7.9x10$^{-4}$ and 4.5x10$^{-4}$ cm$^2$/Vs, respectively. Conductivity and off current ratios of the field applied sample to the reference sample are 2.6 and 110, respectively. Figure 5 shows source current vs. gate voltage characteristics of the two samples. Source current reaches to zero when the gate voltage is zero for the reference sample (non-field), that of the field-applied sample is, however, in on-state even when the gate voltage is 20 V. This phenomenon indicates that the

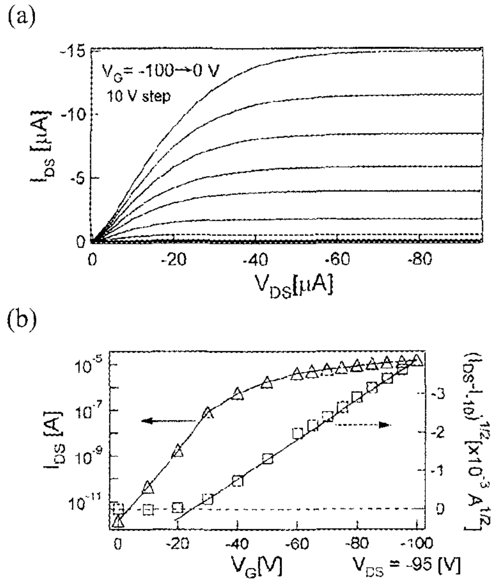


Fig. 3 Typical current voltage characteristics of P3HT-FET. ($L$=20μm, $W$=5mm). (a) is $I_{DS}$-$V_{DS}$ characteristics and (b) is $I_{DS}$-$V_G$ characteristics.

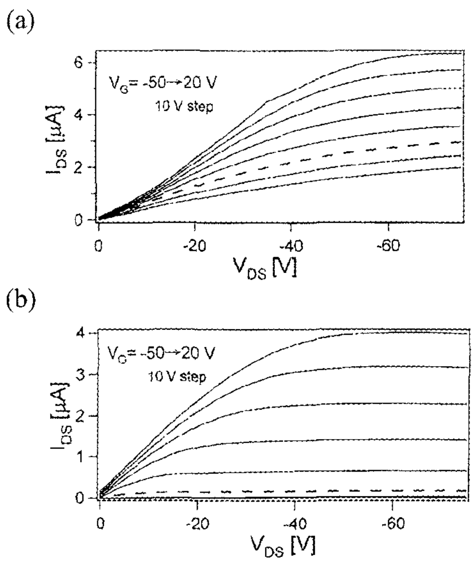


Fig. 4 The $I_{DS}$-$V_{DS}$ characteristics of (a) field-applied sample and (b) reference sample. Doted lines show the $I_{DS}$-$V_{DS}$ characteristic when $V_G$ = 0 V.

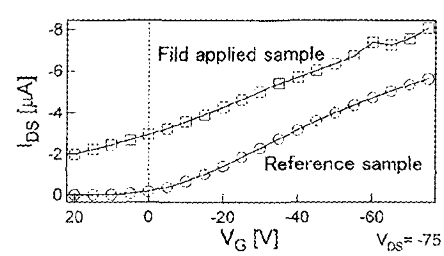


Fig. 5 The current-gate voltage characteristics of field-applied sample (□) and control sample (○).

Table I Electric field strength dependence of device parameters

| Field strength | 1kV/cm | 5kV/cm |
|---|---|---|
| L | 100μm | 100μm |
| σ ratio | 76 | 1.2 |
| μ ratio | 2.0 | $8.7 \times 10^{-4}$ |
| n ratio | 38 | 1300 |

Table II Channel length dependence of device parameters

| Field strength | 1kV/cm | |
|---|---|---|
| L | 50μm | 100μm |
| σ ratio | 330 | 76 |
| μ ratio | 1.0 | 2.0 |
| n ratio | 330 | 38 |

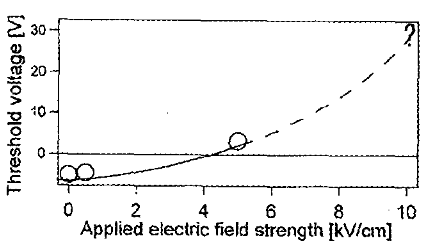


Fig. 6 The field strength dependence of FET threshold voltage.

reference sample is normally-off type and the field-applied sample is normally-on type. Applying electric-field could change the FET operational mode. It is confirmed that the two types of characteristic of P3HT-FET, with different threshold voltages, can be obtained with applying-field casting method.

Table I shows the electric field strength dependence at $L$ = 100 μm. These values in the table are device parameter ratio of the field-applied sample to the reference sample, where σ, μ and n are the conductivity, the mobility and the carrier concentration of P3HT-FETs, respectively. The carrier concentration, n, is given by

$$\sigma = en\mu \qquad (1)$$

where e is the elementary charge. All the parameters increase at 1 kV/cm electric field compared to those of reference samples. Applying an electric field of 1 kV/cm can make the performance of a P3HT-FET enhanced. On the other hand, conductivity increases and the mobility decreases drastically at a field of 5 kV/cm. The ratio of mobility has a large margin of error because the mobility at a field of 5 kV/cm is too low. The drastic decrement of the ratio of the mobility results in the drastic increment of the ratio of the carrier concentration. A lower strength of the electric field can make the performance of a FET enhanced and a higher strength of electric field can make the conductance enhanced. It is confirmed that P3HT layer having an arbitrary characteristic can be obtained with a particular electric field strength in the applying-field casting method.

Figure 6 shows the field strength dependence of threshold voltage. The shift of threshold voltage is large for a strong electric field. This indicates that the FET with a controllable threshold voltage can be obtained using this method. With these results, it is confirmed that organic ICs consisting of inverter circuits without level-shift resistance can be realized.

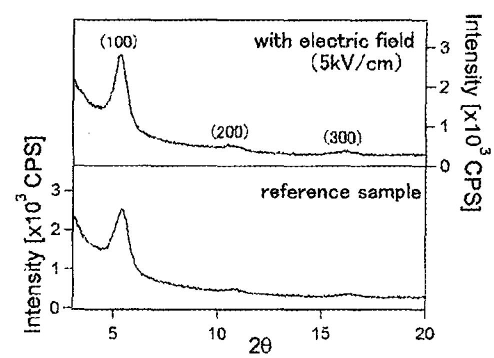


Fig. 7 The XRD pattern of field-applied sample (upper) and reference sample (lower).

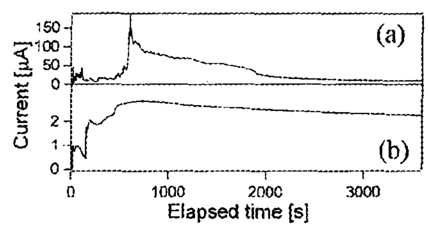


Fig. 8 The current variation during film growth depending on field strength. (a) is at 5kV/cm and (b) is at 1kV/cm.

Table II shows the dependence of device parameters on channel length at 1 kV/cm. The sample having a shorter channel length is more sensitive to the electric field than that having longer one. Since there is a much thinner gate oxide layer (300 nm) compared to the channel length, the electric field is more effective in the active area with a shorter channel length for same electric field strength.

Figure 7 shows the XRD pattern of reference and field-applied sample fabricated simultaneously on different substrates. The first, second and third diffraction peaks of P3HT appear for both the samples, indicating the existence of a highly ordered layer. These patterns indicate that the degree of the molecular ordering is almost same. The peak positions coincide with P3HT lattice parameter, a = 1.6 nm, reported previously [8]. It is confirmed that the field-applied samples have a high molecular ordering parallel to the substrate compared to the reference samples.

Figure 8 shows the current variation during the film formation, which is related to the film growth process. There is a difference in the film growth processes depending upon the electric field strength. Current sharply increases at the threshold point and then gradually decreases. This sharp rise in current indicates that the electrodes are connected to each other with

P3HT polymer grains. This phenomenon may be closely related to the formation of a molecularly ordered conducting pass.

The results of growth process show the formation of molecularly ordered conducting pass parallel to the electric-field can lead to variations of P3HT-FET characteristics. On the other hand, it may be considerable that ionic impurities in the gate oxide layer or in the P3HT layer may lead to the change in the characteristics. Gate electrode takes the half value (1/2 $V_0$) of the potential difference ($V_0$) between the source and the drain since it is floated during the film growth (Fig.9). By this potential distribution, vertical component of electric field near the source electrode is opposite to that of the drain electrode. Ionic impurities must, therefore, be unevenly distributed depending upon the electric field at the gate oxide layer or in the P3HT layer. The field-applied samples, however, had symmetric characteristics even on exchange of the source and drain electrodes, which means the main reason for the FET characteristics changes is a different factor instead of the ionic impurities effect.

## 4. CONCLUSION

Two types of P3HT-FET were fabricated using applying-field casting method. Reference samples without applying field and field-applied samples showed a characteristic of normally-off type FET and normally-on type FET, respectively. The electric field dependence and the channel length dependence for the device parameters were also confirmed. These results indicate the possibility of fabrication of P3HT-FET having an arbitrary threshold voltage, which can be applied for organic integrated circuits. Although a detailed study of this mechanism is still under investigation, a chain ordering effect is considered to be the main reason these differences in FET characteristics.

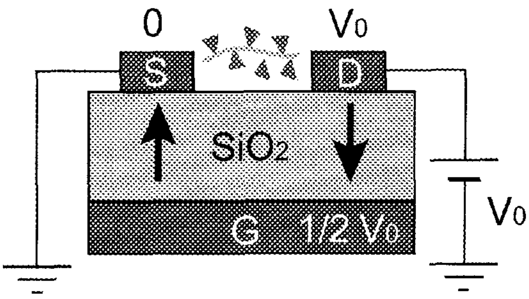


Fig. 9 The schematic illustration showing how to apply an electric-field. The arrows shows electric-field vector. When the gate electrode is floated electrically and $V_0$ is applied between source and drain electrodes, the voltage of gate is 1/2 $V_0$.

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