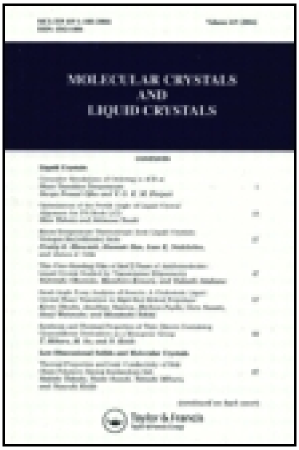

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

New Field-Effect Transistor Using the Semiconducting Plasma-Polymerized Films

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New Field-Effect Transistor Using the Semiconducting Plasma-Polymerized Films

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The preparation and characteristics of the field-effect transistor (FET) based on plasma-polymerized pyrrole (PP-Py) are presented. The electric conductivity of PP-Py was 10^{-9} S/cm and its value was significantly improved to the 10^{-6} S/cm by the thermal treatment of PP-Py under nitrogen atmosphere. The PP-Py based FET displayed the typical enhancement-type FET properties with excellent source current (I_{DS})-drain voltage (V_{DS}) characteristics at various gate voltages (V_G). Field-effect mobility was found to be around 1.1×10^{-4} cm^2/V s, and the threshold voltage of FET performance was -1.2 volt.

Keywords: field-effect transistor, plasma polymerization, pyrrole, thermal treatment, electrical property, organic semiconductor

INTRODUCTION

There has been a considerable progress in the past decade towards the preparation of π-conjugated polymers that exhibit near-metallic conductivity when doped by the electron donors or acceptors.[1] More recently, great research efforts are focused on the fabrication of practical semiconductor devices such as the Schottky diode or FET using these semiconducting π-conjugated polymers. Since the first demonstration of polythiophene FET by Tsumura *et al.*[2] in 1986, polymer-based FET[3–7] has been investigated actively for its potential application as the matrix-array driver of large-area LCD panel.[8] However, it has been pointed out that the semiconducting polymer should possess in advance an excellent processability to form a uniform and thin film over a complex device structure to be useful for such application.[9] In terms of the processability, the plasma polymerization seems to be quite promising since the uniform, dense and thin polymeric films are easily coated on any complex device structure by this process.[10] Therefore, we investigated the

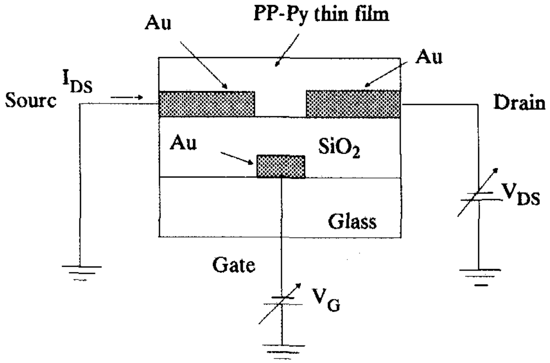

FIGURE 1 Cross-sectional view of the PP-Py based FET device.

methods of preparing the semiconducting polymeric thin films using the plasma polymerization of pyrrole and also of fabricating the new polymer FET device with that film.

EXPERIMENTAL

The plasma polymerization of pyrrole was carried out in a capacitively coupled pyrex bell-jar reactor operating at the 13.56 MHz frequency, as published in other paper.[11] Pyrrole (Aldrich Chemical Co., Ltd) was purified by the vacuum distillation and was degassed by the freeze-pump-thaw method just before the plasma polymerization. The plasma polymerization of pyrrole was carried out for 20 minutes at the discharge power of 5 watts, system pressure of 60 millitorr and the flow rate of 14.5 mg/min. The thermal treatment of plasma-polymerized pyrrole (PP-Py) was effected for 1 hr at 300°C under nitrogen atmosphere. The FT-IR spectra (Mattson Alpha-Centauri Co. Ltd.) of PP-Py deposited on aluminum foil were taken by the external reflection method at the 4 cm^{-1} resolution and 64 scan conditions. The electronic absorption spectra was measured using the Shimadzu UV-VIS 240 spectrophotometer. The optical band gap (E_g^0) was calculated from these spectra according to the theoretical equation [12] suggested for the amorphous semiconductor materials. Perkin Elmer 240C elemental analyzer was used for the determination of C,H,N composition of PP-Py. The cyclic voltammetry (CV) was performed using the potentiostat (Hokuto Denko potentiostat/galvanostat HA301) and function generator (Hokuto Denko HB105). The cell was composed of the PP-Py on the platinum (Pt) plate (1 × 1 cm^2) as a working electrode, Pt counter electrode and Ag/AgCl reference electrode. The electrolyte was 0.1 M $LiClO_4$ in acetonitrile. The structure of FET device is shown schematically in Figure 1. A gold strip of 10 μm width and 2 mm length was coated by sputtering on the glass substrate (2 × 2 cm^2) as the gate electrode. After depositing a 3,000 Å thick SiO_2 insulator by CVD, a couple of gold electrodes were sputter coated for uses as the source and drain electrode respectively. PP-Py was then deposited over there re-

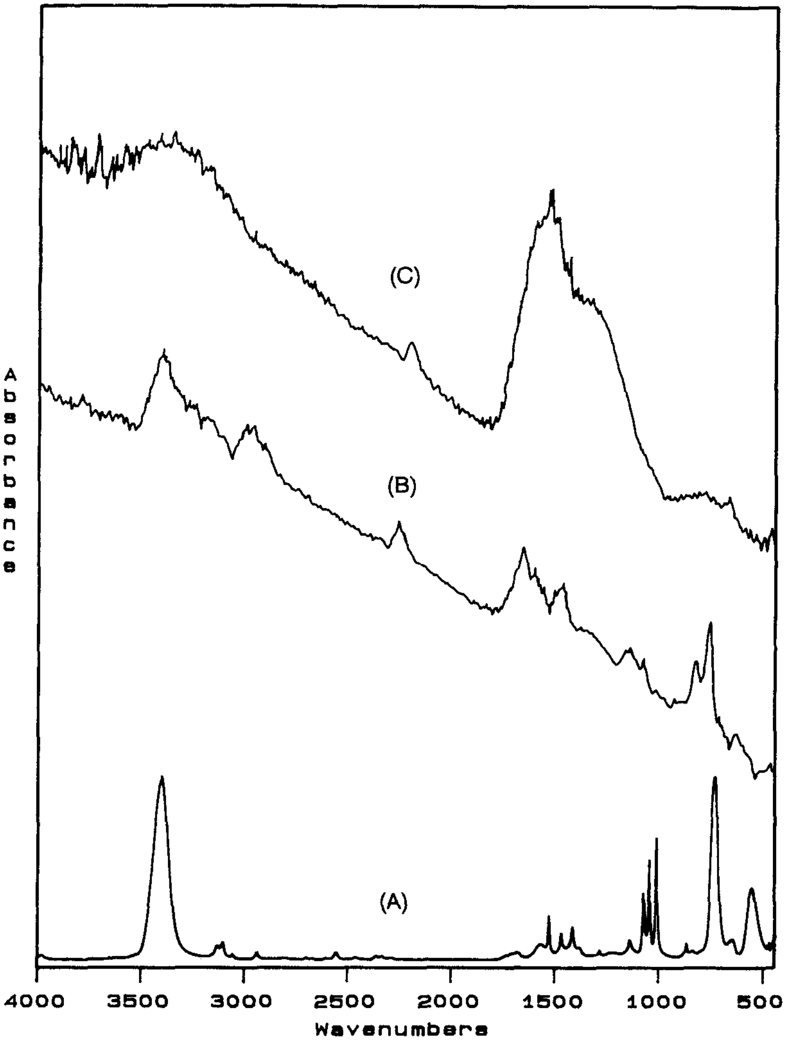

FIGURE 2 FT-IR spectra of pyrrole monomer (A), PP-Py film (B) and thermally treated PP-Py (C). The PP-Py film was obtained at a condition of 5 watts/60 millitorr. The condition for thermal treatment of PP-Py was 300°C for 1 hr under nitrogen atmosphere.

sulting in the PP-Py based FET device with the channel width of 2 mm and the channel length of 10 μm. The device characteristics were measured at room temperature under nitrogen atmosphere by using a Yokogawa Hewlett-Packard 4140B pA meter/dc voltage source.

RESULTS AND DISCUSSION

The FT-IR spectra of pyrrole monomer, PP-Py and thermally treated PP-Py are shown in Figure 2. It is seen that the spectrum of PP-Py is partly composed of the

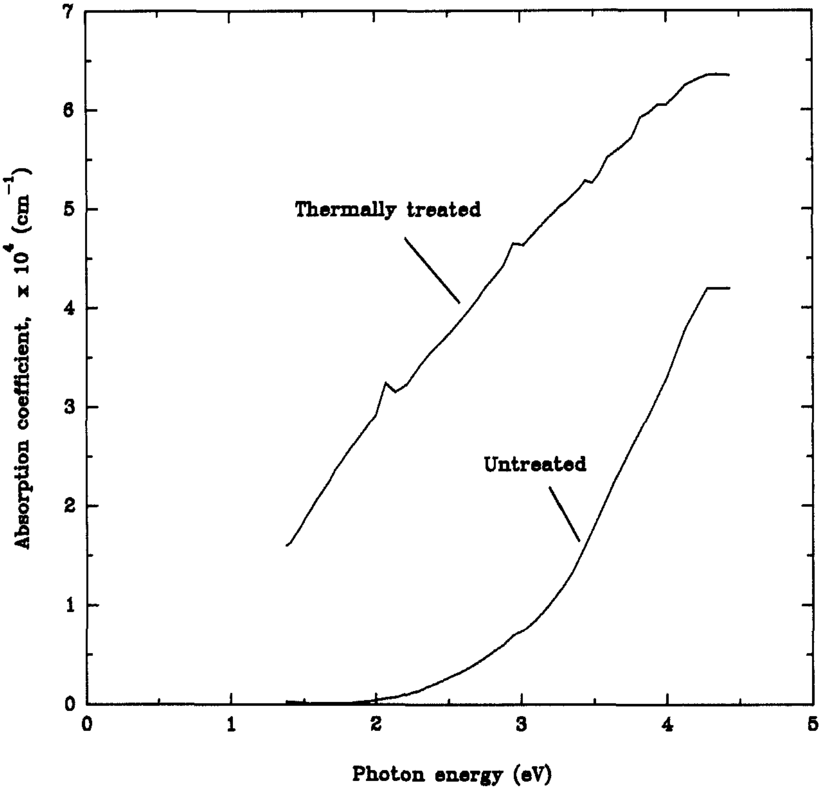

FIGURE 3 UV spectra of PP-Py and thermally treated PP-Py. (The conditions for producing PP-Py and thermal treatment of PP-Py are the same as shown in Figure 2)

characteristic pyrrole peaks such as the N—H stretching at 3400 cm^{-1}, the =C—H in-plane deformation at 1037 ~1096 cm^{-1} indicating aromatic ring breathing of pyrrole[13] and =C—H out-of-plane deformation at 740 cm^{-1}. However, in contrast to the monomer spectrum, PP-Py spectrum is characterized by the several new absorption peaks suggesting the partial ring-opening of pyrrole structure during the plasma polymerization such as the C≡N stretching at 2219 cm^{-1}, aliphatic C—H stretching at around 2900 cm^{-1} and unsaturated C=C or C=N stretching at around 1613 ~ 1622 cm^{-1}. It suggests that plasma-activation of pyrrole seems to proceed by the ring opening and hydrogen detachment reaction simultaneously.[14] In the case of the thermally treated PP-Py, the peak absorption at 1613 ~ 1622 cm^{-1} indicating the conjugated structure is strongly increased as shown in Figure 2. The elemental composition of C,H,N in the PP-Py was found to be $C_{4.12}H_{4.10}N_{1.0}$ in contrast to $C_4H_5N_1$ of monomer pyrrole. Comparing these compositions, we find that the C/N ratio of monomer is almost preserved at the PP-Py structure, however H/N ratio of PP-Py is less than that of monomer possibly supporting the complex activation process.[15] According to the unsaturated double bond character of PP-Py (Figure 2(b)), the band edge of electronic absorption is fairly low as shown in

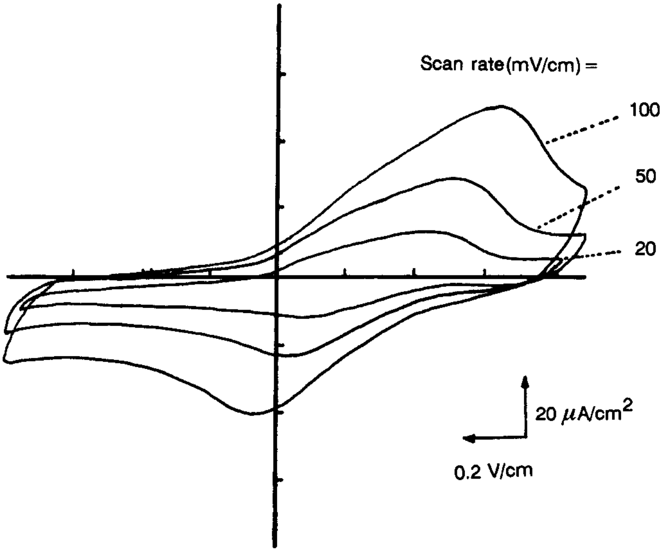

FIGURE 4 Cyclic voltammogram of the thermally treated PP-Py film (electrolyte solution: 0.1 M $LiClO_4$/acetonitrile, reference electrode: Ag/AgCl, working and counter electrode: Pt plate respectively).

Figure 3. The optical band gap calculated from this spectrum was found to be 2.4 eV. Electric conductivity of the PP-Py film was 2×10^{-9} S/cm by the measuring the current-voltage characteristics of Au/PP-Py/Au sandwich cell. The PP-Py film was quite uniform, thin and semiconducting, however, it was too soft as to be scratched easily. Also, the electrical properties were subjected to change by air oxidation. To solve these problems, we thought that thermal treatment of PP-Py might stabilize the film properties. Actually, the thermal treatment of PP-Py under nitrogen atmosphere showed a favorable result. The thermally treated films were so dense that it was very difficult to detach from the substrate even by the razor blade. Also it was found that conductivity of PP-Py was significantly improved to 5×10^{-6} S/cm and its optical band gap was changed to about 1.0 eV by the thermal treatment of the PP-Py. The change of E_g^0 and conductivity of PP-Py may be resulted from the enhanced conjugated structure by the thermal treatment. Since the untreated PP-Py film was soluble in $LiClO_4$/acetonitrile, the CV measurement was carried out using the thermally treated PP-Py films which was insoluble and stable in that electrolyte system (Figure 4). It is evident that the thermally treated PP-Py shows a well-defined reversible electrochemical reaction. The FET device with the thermally treated PP-Py film as the semiconductor material showed a typical enhancement-type FET characteristics. Figure 5 shows the source current as a function of drain voltage at various gate voltages. It is seen that the source current is greatly enhanced when the negative bias voltage is applied to the gate electrode, however, this current is somewhat reduced when the positive voltage is applied to the gate. It is apparent that the device performance is fairly well-defined and the PP-Py thin film layer is p-type semiconductor. It is seen that the I_{DS} increases

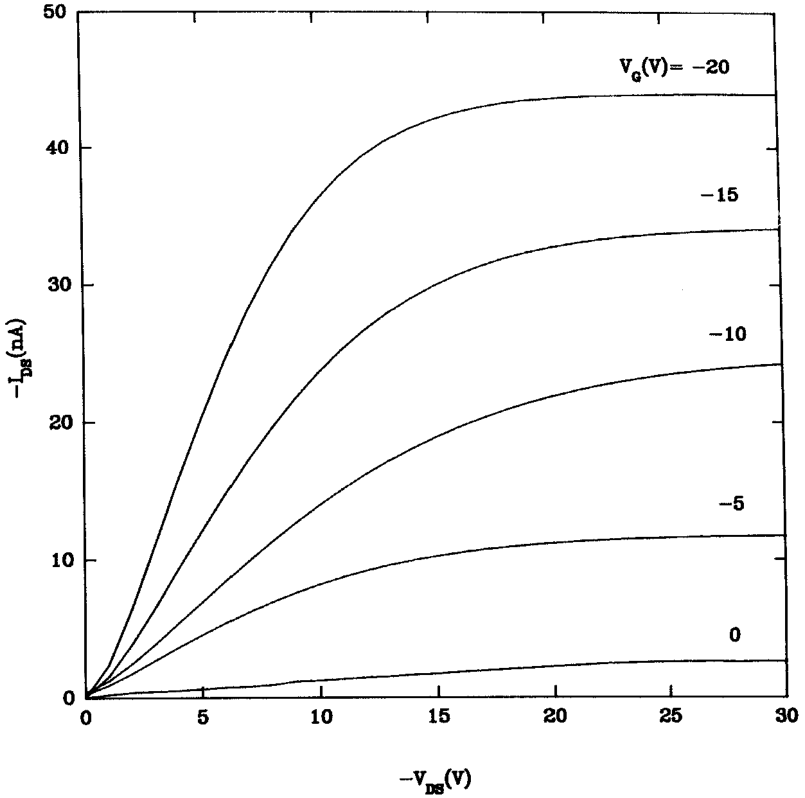

FIGURE 5 Current-voltage characteristics of a PP-Py based IG-FET for different values of the gate voltage. (PP-Py was thermally treated as the same condition of Figure 2)

almost linearly with V_{DS} then saturates to some constant value. Also the I_{DS} value increases significantly according to the magnitude of negative V_G value, which indicates the p-type character of thermally treated PP-Py film. The V_G control over the I_{DS} saturation value is excellent. By plotting the square root of saturated value of I_{DS} against V_G in Figure 6, the field-effect mobility (μ) is found to be around 1.1×10^{-4} cm^2/Vs and the threshold voltage of FET performance is -1.2 volt according to the method of Assadi *et al.*[16]

CONCLUSIONS

The semiconducting organic film of 10^{-6} S/cm conductivity was prepared by the plasma polymerization of pyrrole followed by the thermal treatment under nitrogen. The insulated-gate FET device was successfully fabricated using this film as the active semiconductor. The fabricated device showed a well-defined p-type enhancement FET behavior with -1.2 V threshold voltage. The field-effect mobility of semiconducting layer was calculated to be around 1.1×10^{-4} cm^2/Vs.

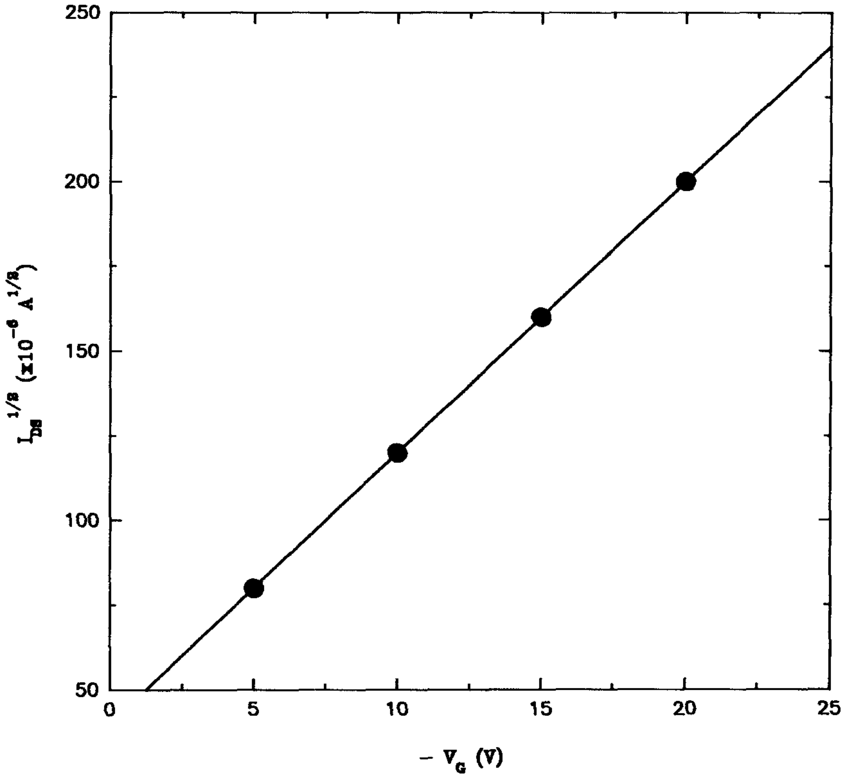

FIGURE 6 $I_{DS}^{1/2}$ versus V_G plot of the PP-Py based IG-FET.

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