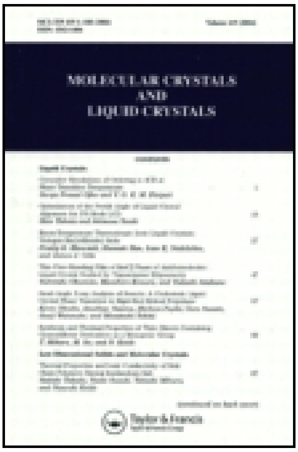

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MACROMOLECULAR ELECTRONIC DEVICE

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Abstract A thin-film transistor (TFT) with high carrier mobility has been fabricated using poly(2,5-thienylenevinylene)(PTV) as semiconductor. The carrier mobility has been obtained to be 0.22cm^2/Vsec, which is in the same level as that of amorphous silicon TFT. It has been indicated that the enlargement of the π-conjugation length is crucial for the improvement of the carrier mobility. It has been also demonstrated that the molecular orientation is another important factor in terms of the device characteristics.

INTRODUCTION

Thin film transistors(TFTs) are one of the most commercially promising applications for deposited semiconducting films.[1] It is well known that amorphous silicon (a-Si) TFTs are used in large-area liquid-crystal displays where each TFT is arranged at every pixel for switching liquid crystals. Several hundreds of thousand TFTs with defect-free have to be fabricated on each panel. On the other hands, a plenty of efforts have been devoted to the fabrication of TFTs with organic semiconductors since the first demonstration of electropolymerized polythiophene TFT.[2] It is because their thin films can be easily prepared by simple methods such as spin coating and vacuum deposition techniques, resulting in the low-cost TFT production. Two types of TFT with organic semiconductors have been reported, that is, insulated-gate and Schottky-gate TFTs until now.

One of the most important parameters to discuss the device characteristics is carrier mobility. The first TFT with a organic semiconductor, polythiophene, gave the carrier mobility of about 10-5 $cm^2/Vsec$.[2] In the last several years, the carrier mobility stayed in the range of 10^{-3} to 10^{-5} $cm^2/Vsec$, which was lower by more than two orders than that (0.1 - 1 $cm^2/Vsec$) of a-Si TFTs.[3] There are primarily two approaches to improve the device characteristics, that is, the carrier mobility. One approach is the purification of semiconducting materials to reduce the carrier scattering by impurities. Lately Garnier et. al. have obtained the same level of the carrier mobility as that of a-Si in the organic insulated-gate TFT with vacuum-deposited α-sexithienyl. The semiconducting material has been purified during deposition.[4] The other approach is to use conducting polymers with large conjugation length. Large π-conjugation length results in wide valence and conduction bands, leading to high carrier mobility.[5]

We have selected the second approach to obtain the high carrier mobility in organic TFTs. In this paper, we will report on the fabrication of the TFT with a spun poly(2,5-thienylenevinylene) film and on the device characteristics with the same order of the carrier mobility as a-Si TFT.[6] The importance of the molecular orientation of the semiconducting materials worked as an active layer will be also demonstrated in the TFTs with α-sexithienyl (6T) prepared under various deposited conditions.

EXPERIMENTAL

The fabricated TFT structure is illustrated in figure 1. Evaporated chromium gate electrode with 115 μm wide, 1 mm long and 100nm thick

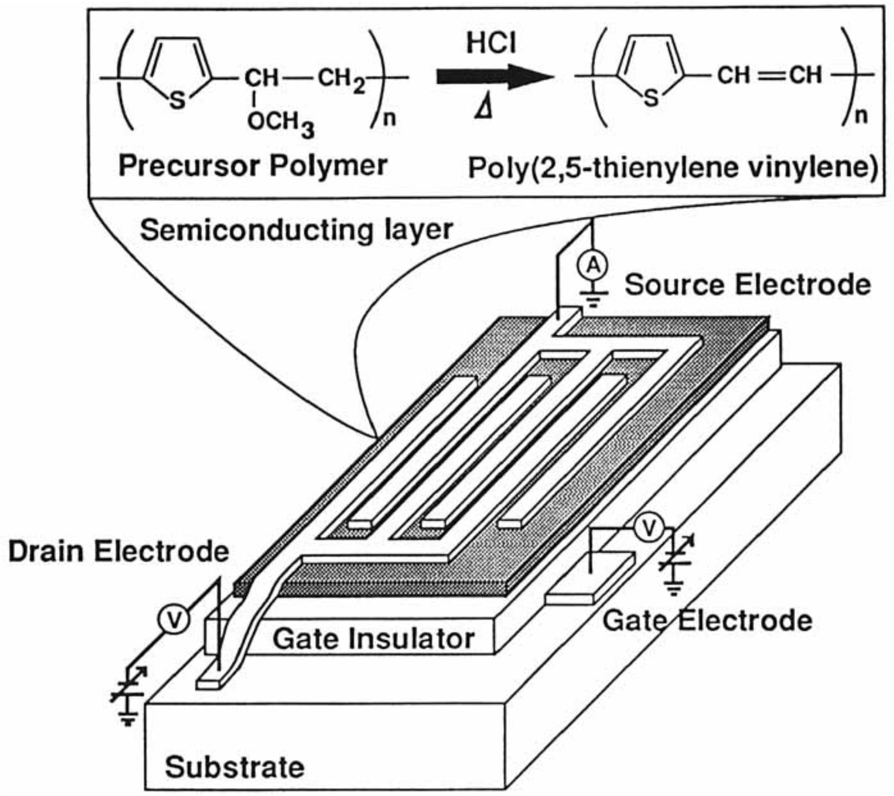

FIGURE 1 Schematic illustration of a fabricated TFT and the conversion reaction scheme from the precursor polymer to PTV.

was patterned on a low-alkaline glass wafer. SiO_2 (500nm thick) worked as gate insulator was electron-beam evaporated onto both the glass and the gate electrode. The precursor polymer (60nm thick) of poly(2,5-thienylenevinylene)(PTV) was spin-coated over the entire surface from its 2 wt%- dimethylformamide solution. The number of repeating unit of the precursor polymer was determined to be ca. 1000 by gel permeation chromatography (GPC) using polystyrene as reference. The precursor film was heated at 200 °C for 5 min under nitrogen stream containing a small amount of hydrochloric acid (HCl) and for 85 min under pure nitrogen atmosphere subsequently. Reaction scheme is also depicted in figure 1. HCl effectively acts as a catalyst for the reaction from the precursor to the PTV polymer during the heat-treatment.[7] A couple of indium-tin oxide (ITO) (100nm thick) electrodes with three fingers worked as source and/or drain electrodes were installed. These are installed by conventional sputtering and photolithographic techniques as a final step to avoid the corrosion of ITO with HCl. The device so fabricated is an insulated-gate TFT with the channel width of 5 mm and the channel length of 5 μm.

6T (about 20nm of the thickness) was deposited on the same TFT substrate as described elsewhere[2] by a molecular-beam deposition technique with a Knudsen cell under 10^{-5}Pa and a conventional evaporation method. The substrate during the deposition was kept at room temperature. The fabricated TFTs are also an insulated-gate one with the channel width of 2 mm and the channel length of 6 μm.

RESULTS AND DISCUSSION

The TFT characteristics with fully converted PTV used as a semiconductor are shown in figure 2. Any doping procedure was not performed because PTV has enough low ionization potential to be automatically p-doped with oxygen in air.[8] The conductivity of the fully converted PTV was evaluated by using the TFT device with floating gate electrode to be in 10^{-5} to 10^{-6} S/cm. The channel current (I_C) flowing from source to drain did not increase so much with drain voltages under no gate bias (normally off). The application of negative gate biases greatly enhanced the I_C. This enhancement of the I_C is due to the accumulation of positive carriers inside the semiconductor toward the interface between SiO_2 and PTV. The saturation (pinch off) of the I_C was also observed under high drain voltage region.

It has been reported that the channel current (I_C) of insulated-gate TFTs in the saturation region is described as followings:[2,9]

$$I_C = \mu W C_{OX}(V_G - V_{th})^2/2L \qquad (1).$$

V_{th} stands for the threshold gate voltage at which the conduction channel begins to form. W, L, C_{OX} and μ represent the channel width, the conduction channel length, the capacitance of the gate insulator and the carrier mobility in the channel, respectively.

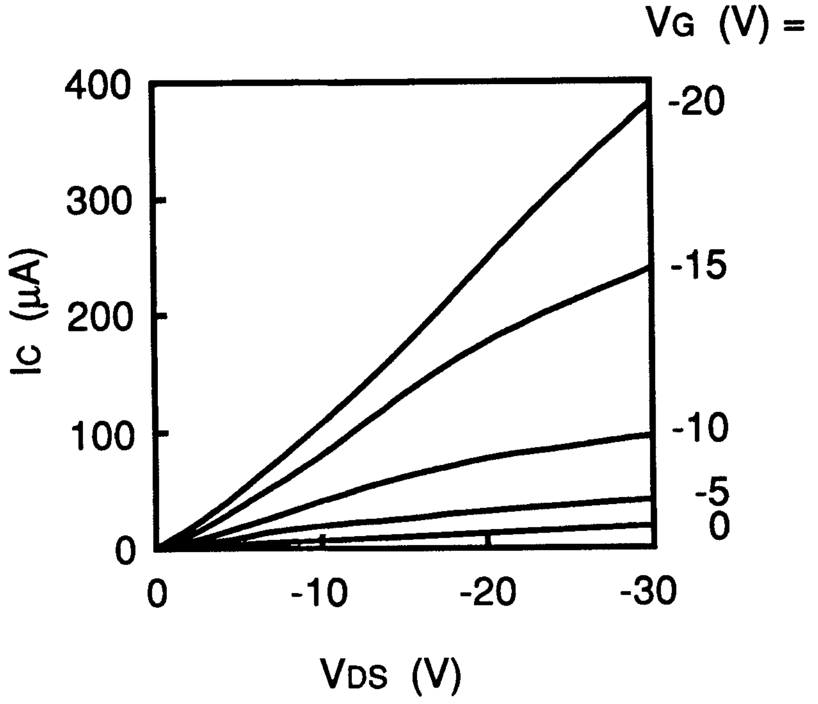

FIGURE 2 Channel current (I_C) vs drain voltage characteristics of the fabricated TFT at various gate voltages (V_G).
The conversion ratio from the precursor to PTV was 98%.

The plots of square root of the I_C against the gate voltage (V_G) for our device with interconnected gate-drain electrodes yielded the straight line in the high $V_{DS}(=V_G)$ region. The carrier mobility was calculated to be 0.22 cm^2/Vsec from the slope and Eq. 1. The obtained carrier mobility is in the same level as those of a-Si TFTs. Since the semiconducting layer in our TFT can be prepared by a simple spin-coating technique, our device has the great advantage in terms of the low-cost fabrication.

The carrier mobility greatly depends on the π-conjugation length of PTV. The carrier mobility was plotted against the conversion ratio in the reaction from the precursor to PTV in figure 3.[10] The intensity ratio of an IR absorption peak at 1095 cm^{-1} assigned to C-O-C stretching mode of the precursor to the peak at 806 cm^{-1} attributed to C-H out-of-plane bending mode in thiophene has been used to evaluate the conversion ratio.[11] The former absorption in the precursor decreased with conversion and almost disappeared in the fully converted film, while the latter peak did not change throughout the reaction.

When the conversion ratio is 4%, the carrier mobility stayed in the order of 10^{-5} $cm^2/Vsec$. The carrier mobility linearly increased with proceeding the conversion finally to reach 0.22 $cm^2/Vsec$ at the conversion ratio of 98% (figure 3). This result indicates that the carrier mobility is proportional to the amount of semiconducting PTV chains converted from its precursor.

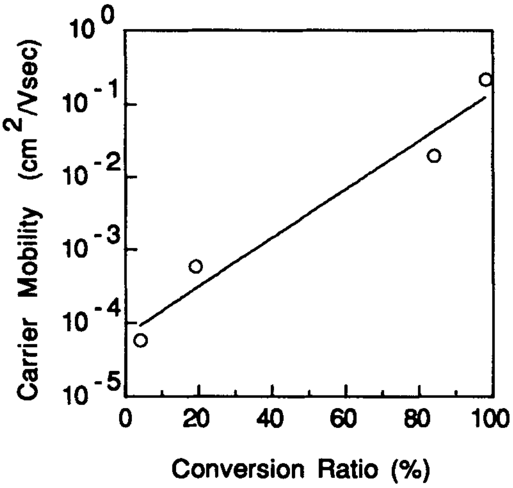

FIGURE 3 Carrier mobility vs the conversion ratio of the reaction from the precursor polymer to PTV.

As the conversion reaction proceeded, a π-π* transition appeared to grow in the visible spectra and the absorption edge shifted to lower energy to be 1.7 eV. The observation of the absorption spectra in the visible region and the peak-shift to lower energy clearly indicate the enlargement of the effective π-conjugation length accompanying with the conversion reaction. It has been, therefore, made clear that the effective π-conjugation length is crucial to enhance the carrier mobility of TFTs with conducting polymers.

Effect of the molecular orientation on the TFT characteristics.

The 6T films were prepared on quartz glass plates by flash evaporation and molecular-beam deposition methods. The UV-VIS absorption spectra of the films are shown in figure 4. The p- or s-polarized light was incident to the surface at the angle of 45° to study the molecular orientation of the films. The large absorption was observed at 3.2~3.5 eV, which was assigned to the π-π* transition.

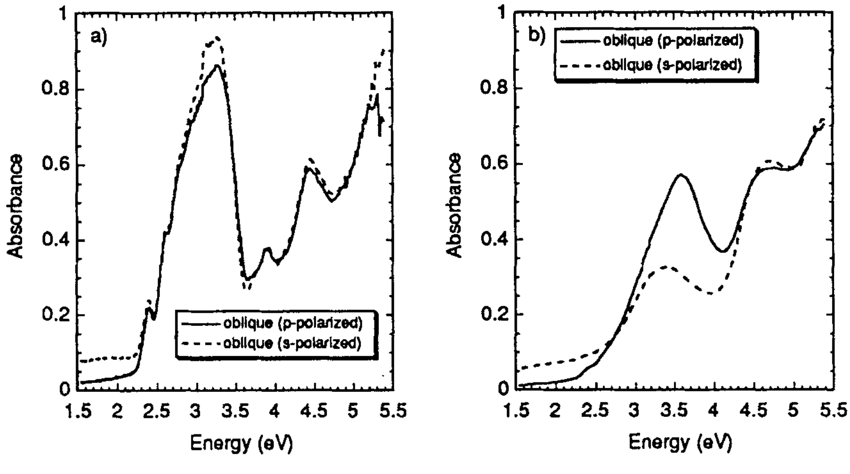

FIGURE 4 UV-VIS absorption spectra for (a) flash-evaporated 6T and (b) molecular-beam deposited 6T films. The incident angle of the p- and s-polarized light was 45°(oblique).

The intensity of the absorption spectra for the flash-evaporated films is almost comparable for both p- and s-polarized light. There is no indication of the molecular orientation. On the contrary, the intensity of the absorption spectra measured with p-polarized light is larger than that observed with s-polarized light for the molecular beam deposited films. The observed dichroism between s- and p-polarized incident light indicates that the dipole moment of the π-π^* transition is relatively aligned along the surface normal comparing with the case of the flash-evaporated films. Since the dipole moment of the π-π^* transition is believed to be along the molecular long axis of 6T, the 6T molecular axis should be directed along the surface normal to some extent for the molecular-beam deposited film.

The device with the flash-evaporated 6T film have been well investigated to be a p-channel and accumulation-mode TFT.[12] The TFT with the molecular-beam deposited films is fabricated to study the effect of the 6T molecular orientation on the device characteristics (figure 5).

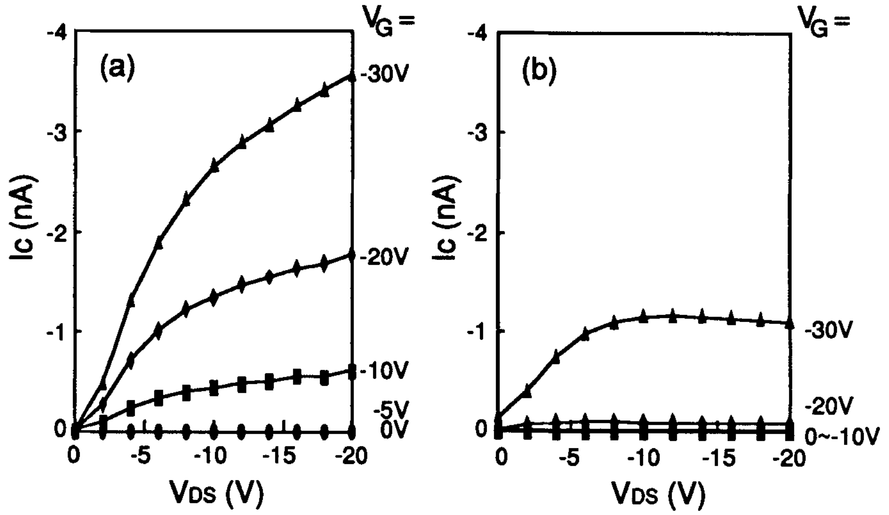

FIGURE 5 Channel current (I_C) vs drain voltage (V_{DS}) characteristics of the fabricated transistors at various gate voltages (V_G). (a) Flash-evaprated 6T and (b) molecular-beam deposited 6T films were used as semiconducting layers.

The TFT with the molecular-beam deposited film gave the smaller channel current. This result clearly indicates that the interchain hopping is a rate-limiting step in the carrier conduction between the source and the drain. If the 6T molecules are completely aligned along the surface normal, every carrier injected from the source have to continue hopping between the neighboring molecules along the electric filed before the arrival at the drain.

The 6T molecules are not aligned along the specific direction in the flash-evaporated film. However, it is considered that the carriers injected from the source can reach faster toward the drain because they have a chance to move inside the 6T molecules other than the hopping. If the 6T molecules in the TFTs could be aligned along the direction from source to drain, the device characteristics would further improve.

CONCLUSION

The TFT with the spun PTV film has been fabricated and has exhibited the carrier mobility comparable to that of a-Si TFTs. The carrier mobility of conducting polymers has been clearly indicated to be linearly proportional to their π-conjugation length. The TFTs with conducting polymers used as semiconductor are one of the most promising alternative to a-Si TFTs. We have also demonstrated the importance of the molecular orientation in organic semiconductor located between source and drain to improve the device characteristics.

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