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Voltage-Induced Infrared Spectra from the Organic Field-Effect Transistor Based on N,N'-bis(3-methylphenyl)-N,N'diphenyl-1,1'-biphenyl-4,4'diamine (TPD)

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Voltage-Induced Infrared Spectra from the Organic Field-Effect Transistor Based on *N,N'*-bis(3-methylphenyl)-*N,N'*-diphenyl-1,1'-biphenyl-4,4'-diamine (TPD)

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The field-effect transistor fabricated with N,N'-bis(3-methylphenyl)-N,N'-diphenyl-1,1'-biphenyl-4,4'-diamine (TPD) on a silicon substrate has shown a p-channel organic field-effect transistor (OFET) operating in the accumulation mode. The hole mobility in the TPD layer has been obtained to be $7.2 \times 10^{-4} \, \mathrm{cm^2 \, V^{-1} \, s^{-1}}$. Gate-voltage-induced infrared absorption from the OFET has been measured in the transmission-absorption configuration by the FT-IR difference-spectrum method. The observed spectra depend on the gate voltage applied. The vibrational Stark effect and the bands originating from the carriers injected into the TPD layer have been observed.

Keywords: infrared spectroscopy; mobility; organic field-effect transistors; TPD

INTRODUCTION

Organic field-effect transistors (OFETs) have made impressive progress over the past 10 years [1]. The schematic device structure of an OFET fabricated with TPD as a semiconductor is shown in Figure 1. The transistor has a metal-insulator-semiconductor (MIS) structure and operates as a capacitor [2]. When a voltage is applied between the source and the gate, a charge is injected into the semiconductor film. Then, the injected charge is accumulated at the insulator-semiconductor interface and forms a conducting channel. Accordingly, a current flows between the source and the drain through the channel when a drain voltage is applied between these electrodes. The

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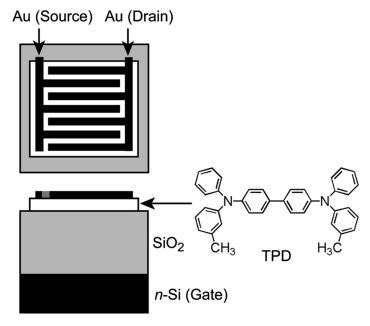


FIGURE 1 Schematic device structure of an OFET based on TPD.

transistor characteristics depend on the density, the distribution, and the mobility of carriers. We have demonstrated that infrared spectroscopy is a powerful tool for the studies of the carriers in OFETs [3,4]. In this paper, we will report the characteristics and the gatevoltage effect on the infrared spectrum of the OFET based on TPD.

EXPERIMENTAL SECTION

Device Fabrication

N-type silicon wafers (1–10 Ω cm, $\langle 100 \rangle$ axis) covered with a thermally grown SiO₂ layer (thickness, ca. 300 or 500 nm) were purchased from Furuuchi Chemical Co. A TPD film (thickness, 100 nm) was formed onto the SiO₂ surface by heat evaporation. Finger-shaped electrodes (thickness, 50 nm) were formed on the TPD layer by the heat evaporation of Au and used as the source and the drain electrodes. The width and the length of each finger were 75 μm and 6 mm, respectively. The number of fingers was 26. The distance between the neighboring fingers was 75 μm. Thus, the length and the total width of the channel were 75 μm and 150 mm, respectively.

Infrared Measurements

Infrared spectra were measured on a Digilab FTS-7000e FT-IR spectrometer equipped with a linearized HgCdTe detector at room temperature. Voltage-induced infrared absorption spectra from the OFET were measured in the transmission-absorption configuration by the FT-IR difference-spectrum method [3]. In this measurement, the interferograms from the device at the voltage of V_1 and V_0 were accumulated and calculated in a normal way by the computer of the spectrophotometer. Thus, we obtained the difference absorbance spectrum between the V_1 and V_0 states.

RESULTS AND DISCUSSION

Device Characteristics

Figure 2 shows the gate-voltage $(V_{\rm G})$ dependence of capacitance per unit area for the OFET with the connection of the source and the drain electrodes (MIS diode). TPD behaves as a p-type semiconductor. In the positive bias region larger than 9 V, the observed capacitance has shown a constant value. The observed capacitance originates from the direct series of the ${\rm SiO_2}$ and TPD capacitors. From the gate voltage of 9 V, the observed capacitance increases and shows a plateau. In this region, positive carriers are accumulated at the TPD-SiO₂ interface. Thus, the threshold voltage [2] is 9 V. Figure 3 describes the

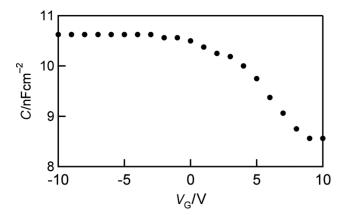


FIGURE 2 Plot of capacitance versus gate voltage ($V_{\rm G}$) measured at 100 Hz for the TPD OFET. The source and the drain electrode are connected with each other.

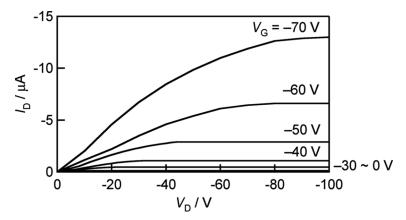


FIGURE 3 Plot of drain current (I_D) versus drain voltage (V_D) at various gate voltages (every 10 V from 0 to -70 V) for the TPD OFET.

relation between the measured drain current $(I_{\rm D})$ and drain voltage $(V_{\rm D})$. The observed characteristics are typical $I\!-\!V$ curves for a p-channel OFET operating in the accumulation mode. They show saturation behavior. The hole mobility $\mu_{\rm h}$ has been calculated in the saturation regime by using the standard FET Eq. (1). The obtained hole mobility and the threshold voltage were $7.2\times 10^{-4}\,{\rm cm}^2\,{\rm V}^{-1}{\rm s}^{-1}$ and $-30\,{\rm V}$, respectively.

Voltage-Induced Infrared Spectra

The spectrum of the OFET is shown in Figure 4a. The observed bands have been attributed to TPD. Figure 4b–4d show the gate-voltage-induced difference spectra from the OFET. Since the drain and the source are connected with each other in all the measurements, the device operates as an MIS diode. In general, vibrational spectra depend on the external electric field; this is called the vibrational Stark effect (VSE) [5]. In the difference spectrum between the gate voltages of 50 and 10 V (Fig. 4c), the observed bands are attributable to VSE, because carriers are not injected into the TPD layer at 50 and 10 V. In the -80/80 V difference spectrum (Fig. 4d), VSE may be cancelled out, because the similar electric field is applied to the TPD layer at -80 and 80 V. Thus, the observed bands are mainly attributable to positive carriers injected into the TPD layer. In the -30/10 V difference spectrum (Fig. 4b), the observed bands have been attributed to the positive carriers and VSE.

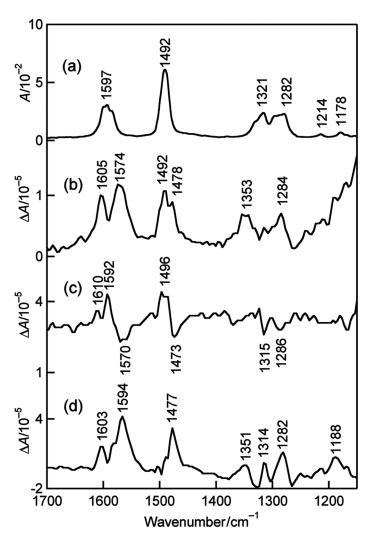


FIGURE 4 (a) Infrared spectrum of the TPD OFET and (b-d) gate-voltage induced infrared difference spectra from the OFET. Difference spectra (b) between -30 and $10\,V$, (c) 50 and $10\,V$, and (d) -80 and $80\,V$.

Estimation of Carrier Sheet Density

The radical cation of TPD has been prepared by the oxidation with iron(III) chloride in a dichloromethane (CH_2Cl_2) solution. The infrared spectra of TPD and its radical cation in the CH_2Cl_2 solutions are shown in Figure 5a and 5b, respectively. The molar absorption

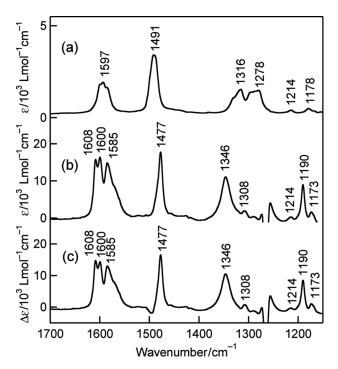


FIGURE 5 Infrared spectra of (a) TPD and (b) the radical cation of TPD in dichloromethane solutions and the difference spectrum between (b) and (a).

coefficient of the 1477-cm⁻¹ band of the radical cation is 1.72×10^4 L mol⁻¹ cm⁻¹, whereas that of the 1491-cm⁻¹ band of TPD is 3.08×10^3 L mol⁻¹ cm⁻¹. Figure 5c shows the difference between the spectra of the radical cation and TPD. The voltage-induced spectrum from the OFET (Fig. 4d) is essentially similar to this difference spectrum. The cross section σ of the 1477-cm⁻¹ band have been obtained to be 6.58×10^{-17} cm² from the following equation:

$$\sigma[{\rm cm}^2] = \frac{(\ln 10) 10^3 \varepsilon}{N_{\rm A}} \approx 3.824 \times 10^{-21} \varepsilon \, [{\rm Lmol}^{-1} {\rm cm}^{-1}] \eqno(1)$$

where $N_{\rm A}$ is Avogadro's number. Since carriers are accumulated at the TPD-SiO₂ interface, the absorbance of an infrared band due to carriers, A, can be expressed by the cross section of the band, σ , and the carrier sheet density, N:

$$A = (\log e)\sigma N \approx 0.4343\,\sigma N. \tag{2}$$

The absorbance of the voltage-induced 1477-cm^{-1} band (Fig. 4d) is 3.8×10^{-5} absorbance unit at a gate voltage of $-80\,\mathrm{V}$. Therefore, N at $-80\,\mathrm{V}$ has been obtained to be $1.3 \times 10^{12}\,\mathrm{cm}^{-2}$ by using Eq. (2).

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