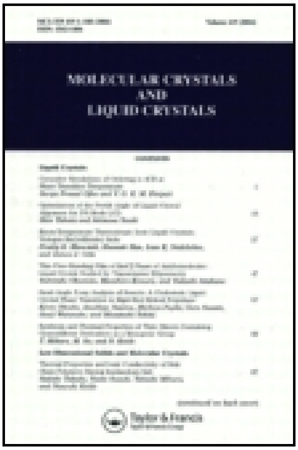

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

High Performance n-Channel Organic Field-Effect Transistors Based on N,N′-Dioctyl-3,4,9,10-Perylene Tetracarboxylic Diimide

Yoshinobu Hosoi [a] & Yukio Furukawa [a]
[a] Department of Chemistry, School of Science and Engineering, Waseda University, Shinjuku-ku, Tokyo, Japan

To cite this article: Yoshinobu Hosoi & Yukio Furukawa (2006): High Performance n-Channel Organic Field-Effect Transistors Based on N,N′-Dioctyl-3,4,9,10-Perylene Tetracarboxylic Diimide, Molecular Crystals and Liquid Crystals, 462:1, 37-43

To link to this article: http://dx.doi.org/10.1080/15421400601009369

Mol. Cryst. Liq. Cryst., Vol. 462, pp. 37–43, 2007
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400601009369

High Performance n-Channel Organic Field-Effect Transistors Based on N,N′-Dioctyl-3,4,9,10-Perylene Tetracarboxylic Diimide

Yoshinobu Hosoi
Yukio Furukawa
Department of Chemistry, School of Science and Engineering, Waseda University, Shinjuku-ku, Tokyo, Japan

The organic field-effect transistors based on N,N′-dioctyl-3,4,9,10-perylene tetracarboxylic diimide have been fabricated on the pristine SiO_2/Si substrate whose surfaces are modified with hexamethyldisilazane (HMDS) and octadecyltriethoxysilane (OTES). The surface modifications have enhanced the electron mobility and on/off ratio, and decreased the threshold voltage. The atomic force microscopy and infrared spectroscopy studies have revealed no differences in the morphology and molecular orientation of the thin films on the pristine and the HMDS-treated substrates.

Keywords: atomic force microscopy; infrared spectroscopy; N,N′-dioctyl-3,4,9,10-perylene tetracarboxylic diimide; organic field-effect transistor

INTRODUCTION

Organic field-effect transistors (OFETs) are of great interest for their potential applications in low cost, flexible, and large area devices [1]. N-type as well as p-type organic semiconductors are essential components of bipolar transistors and complementary circuits. Although high-performance p-type semiconductors have been reported, few compounds have been found to function as n-type semiconductors. Recently, several groups [2–5] have reported that N,N′-dialkyl-3,4,9,10-perylene

This work was supported by a Grant-in-Aid for Scientific Research (A) (16205004) from JSPS and the 21COE “Practical Nano-Chemistry” from MEXT.

Address correspondence to Yoshinobu Hosoi, Department of Chemistry, School of Science and Engineering, Waseda University, Shinjuku-ku, Tokyo, 169-8555, Japan. E-mail: hosoi@aoni.waseda.jp

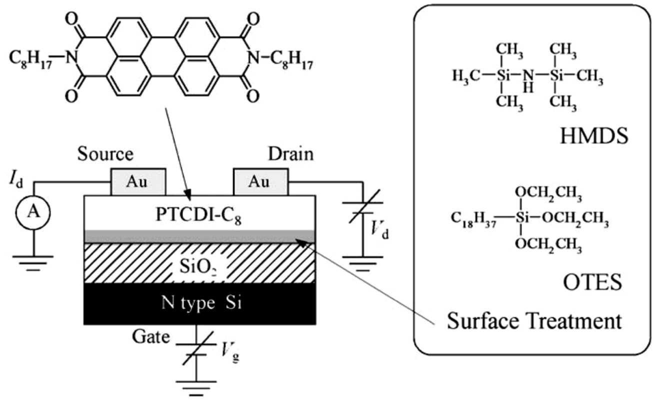

FIGURE 1 Schematic device structure of an OFET based on PTCDI-C_8 and structural formulas of chemical reagents.

tetracarboxylic diimides are n-type compounds with high electron mobilities.

In the present study, we have fabricated the n-channel OFETs with N,N′-dioctyl-3,4,9,10-perylene tetracarboxylic diimide (PTCDI-C_8), as shown in Figure 1. our study focuses on the modification of the SiO_2 surface with hexamethyldisilazane (HMDS) or octadecyltriethoxysilane (OTES) by a chemical vapor deposition process [6]. We have found the dramatic improvement of the transistor performance upon the surface modifications. In addition, the morphology and the molecular orientation of the thin films of PTCDI-C_8 on the pristine and the HMDS-modified SiO_2 surface have been investigated by atomic force microscopy (AFM) and infrared spectroscopy.

EXPERIMENTAL

Figure 1 shows the schematic structure of the device prepared in this study. A highly doped n-type silicon wafer (0.02 Ω cm, ⟨100⟩ axis) covered with a thermally grown SiO_2 layer (thickness, ca. 500 nm) was purchased from Furuuchi Chemical Co. The substrate was immersed in a 1:1 mixture of concentrated H_2SO_4 and H_2O_2 (30% water solution) for 10 min. The cleaned substrate was kept in a Teflon® container including neat HMDS at room temperature for more than 12 h, or including neat OTES at 150℃ for 3 h. PTCDI-C_8 was synthesized according to the previous method [7] and purified by vacuum sublimation. A 40-nm thick PTCDI-C_8 film was prepared by vacuum vapor deposition at a rate of 0.5 nm/min. Top-contact interdigital source and drain electrodes were made with gold through a shadow mask by vacuum vapor deposition. The thickness of the electrodes ranged between 30 and 40 nm. The length (L) and width (W) of the channel were 50 μm and 60 mm, respectively.

Transistor characteristics were measured at a pressure below 1×10^{-2} Pa using two Keithley Model 6487 picoammeter/voltage source units. An electron mobility (μ_e) and a threshold voltage (V_{th}) at the saturation region were derived in a standard manner by the following equation [8]:

$$I_{d.sat} = \frac{W\mu_e C}{2L}(V_g - V_{th})^2 \tag{1}$$

where $I_{d,sat}$, C, and V_g are the drain current at the saturation region, the capacitance per unit area of the SiO_2 gate dielectric, and the gate voltage, respectively.

AFM and infrared measurements were performed for the thin PTCDI-C_8 films prepared on an n-type silicon substrate (1–5 Ωcm, ⟨100⟩ axis) covered with a thermally grown SiO_2 layer (thickness, ca. 500 nm). This silicon wafer was purchased from Sansho Shoji Co., Ltd. The modification of the SiO_2 surface with HMDS was described above. Tapping-mode AFM images were recorded on a Digital Instruments Dimension 3100 AFM. Infrared spectra of the films were measured in a transmission-absorption configuration on a Varian FTS-7000e FT-IR spectrometer equipped with a linearized HgCdTe detector. Pristine and HMDS-treated substrates were used as references.

RESULTS AND DISCUSSION

Transistor Characteristics

Figure 2(a) shows the output characteristics of the OFET based on the HMDS-treated substrate. The observed are the typical I-V curves for an n-channel OFET operating in the accumulation mode, showing the clear saturation region. The transfer characteristics at the saturation region for the OFETs with the pristine, HMDS-treated, and OTES-treated substrates are shown in Figure 2(b). The HMDS- and OTES-treated devices show much larger I_d in the range of the positive V_g than the pristine one. We have defined the on/off ratio as the ratio of I_d between $V_g = 50$ V and $V_g = 0$ V. Table 1 summarizes the obtained μ_e, on/off ratio, and V_{th} of each device. The surface modifications have increased μ_e and on/off ratio, and decreased V_{th}. The highest electron mobility is $0.46\,cm^2V^{-1}s^{-1}$ for the OTES-treated device.

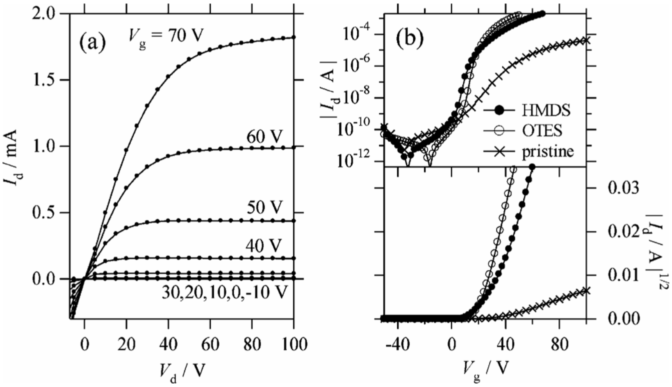

FIGURE 2 (a) Output characteristics for the PTCDI-C_8 OFET based on the HMDS-treated substrate and (b) Transfer characteristics for the OFETs based on the HMDS-treated, OTES-treated, and pristine substrates.

Morphology and Molecular Orientation

The AFM images of the PTCDI-C_8 films on the HMDS-modified surfaces with the thicknesses of 1.0, 2.5, and 10 nm are shown in Figures 3(a), (b), and (c), respectively. The 1.0 nm film exhibits many small grains (100–200 nm). As the thickness increases, the grains grow along the substrate surface and coalesce with the neighboring grains. Figure 3(b) indicates that the first monolayer is almost formed with a few grains on it at the thickness of 2.5 nm. Figure 3(c) shows the successive formation of the multilayer in the growth process similar to the first monolayer. The average roughness (R_a) is 0.90 nm. A smooth film without deep grain boundaries is formed. The AFM image of the PTCDI-C_8 film at the thickness of 2.5 nm in Figure 3(d) shows an almost filled first monolayer similar to that on the HMDS-modified surface.

Figure 4(a) shows the infrared spectra of the PTCDI-C_8 films on the HMDS-treated substrates at the region from 2750 to 3050 cm^{-1}. Three bands are observed at 2857, 2929, and 2956 cm^{-1}. These bands are

TABLE 1 Electron Mobilities, on/off Ratios, and Threshold Voltages Determined for n-Channel OFETs based on PTCDI-C_8

	$\mu_e/cm^2V^{-1}s^{-1}$	on/off ratio	V_{th}/V
HMDS-treated	2.9×10^{-1}	10^6	28
OTES-treated	4.6×10^{-1}	10^7	21
Pristine	2.5×10^{-3}	10^4	36

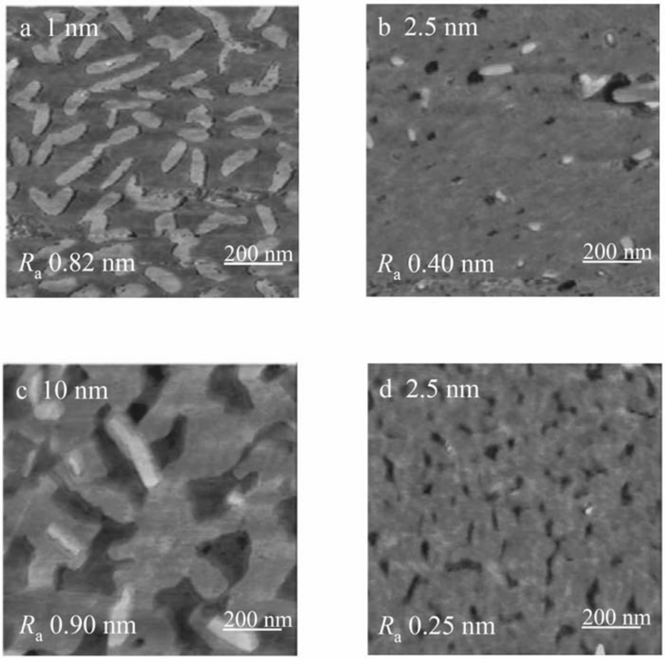

FIGURE 3 AFM images of the PTCDI-C_8 films at the thicknesses of (a) 1.0 nm, (b) 2.5 nm, (c) 10 nm on the HMDS-treated substrate, and (d) AFM image of the 2.5 nm PTCDI-C_8 film on the pristine substrate.

assigned to the CH_2 symmetric stretching vibration, the CH_2 asymmetric stretching vibration, and the CH_3 asymmetric stretching vibration, respectively. The relative intensities of 2857 and 2956 cm^{-1} bands with respect to the 2929 cm^{-1} band are different between the 1 nm and 10 nm thick films. In the transmission configuration, vibrational modes whose transition dipole components are parallel to the substrate are enhanced, while those perpendicular to the substrate are suppressed. The observed changes in relative intensity indicate that PTCDI-C_8 molecules in the first monolayer take an orientation different from that in the multilayer. The same changes in the relative intensities of the 2857 and 2956 cm^{-1} bands are also observed for the films formed on the pristine substrate (Fig. 4(b)). Thus, no difference in the molecular orientations of the PTCDI-C_8 films on the pristine and the HMDS-modified surfaces is found.

Our AFM and infrared results have demonstrated that the morphology and the molecular orientation are similar for the pristine

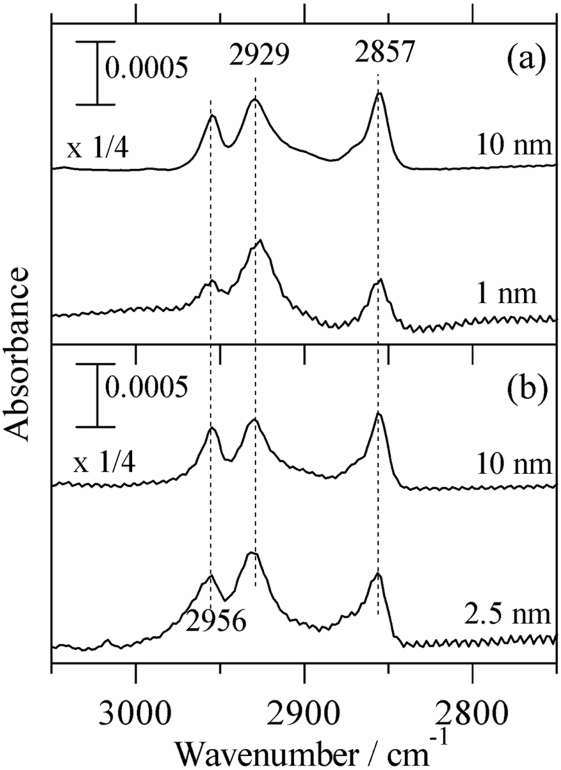

FIGURE 4 Infrared spectra of the PTCDI-C_8 thin films at the thicknesses of 1.0 nm and 10 nm on (a) the HMDS-treated and (b) the pristine substrates.

and the HMDS-treated devices. Recently, Chua *et al*. [9] have showed that SiOH silanol groups on a pristine SiO_2 surface trap electrons. The surface treatments eliminating silanol groups may provide the high performance of the OFETs.

SUMMARY

The OFETs based on PTCDI-C_8 with a high electron mobility have been made by modifying the SiO_2 surface with HMDS and OTES. The PTCDI-C_8 films grow in the similar manner on both the pristine and HMDS-modified surfaces. The molecular orientation in the first monolayer is different from that in the multilayer. Probably, the surface modifications that eliminate electron trap sites provide the high-performance n-channel OFETs.

REFERENCES

[1] Dimitrakopoulos, C. D. & Malenfant, P. R. L. (2002). *Adv. Mater.*, *14*, 99.

[2] Malenfant, P. R. L., Dimitrakopoulos, C. D., Gelorme, J. D., Kosbar, L. L., Graham, T. O., Curioni, A., & Andreoni, W. (2002). *Appl. Phys. Lett.*, *80*, 2517.

[3] Chesterfield, R. J., McKeen, J. C., Newman, C. R., Frisbie, C. D., Ewbank, P. C., Mann, K. R., & Miller, L. L. (2004). *J. Appl. Phys.*, *95*, 6396.

[4] Chesterfield, R. J., McKeen, J. C., Newman, C. R., Ewbank P. C., Filho, D. A. S., Brédas, J. L., Miller, L. L., Mann, K. R., & Frisbie, C. D. (2004). *J. Phys. Chem. B*, *108*, 19281.

[5] Unni, K. N. N., Pandey, A. K., & Nunzi, J. M. (2005). *Chem. Phys. Lett.*, *407*, 95.

[6] Sugimura, H., Ushiyama, K., Hozumi, A., & Takai, O. (2000). *Langmuir*, *16*, 885.

[7] Demmig, S. & Langhals, H. (1988). *Chem. Ber.*, *121*, 225.

[8] Sze, S. M. (1981). *Physics of Semiconductor Devices*, 2nd ed. Wiley-Interscience: New York, 374.

[9] Chua, L. L., Zaumseil, J., Chang, J. F., Ou, E. C. W., Ho, P. K. H., Sirringhaus, H., & Friend, R. H. (2005). *Nature*, *434*, 194.