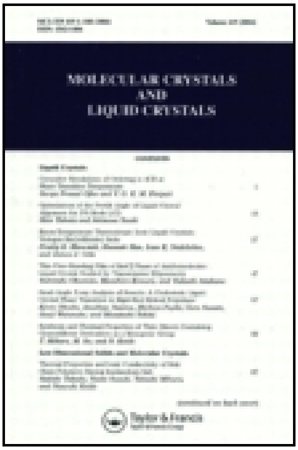

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Organic Field-Effect Transistors Using Polydiacetylene Derivatives as an Active Layer

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Organic Field-Effect Transistors Using Polydiacetylene Derivatives as an Active Layer

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To enhance the field-effect mobility, we tried to control the interchain distance (or packing density of polymer chains) in polydiacetylene thin films by changing the side chain length of diacetylene monomers. We selected five different alkyl chain lengths of diacetylene monocarboxylic acid. An OFET device was prepared by a vacuum deposition of diacetylene monomer, followed by a photopolymerization under Xe-lamp excitation (bottom-contact type device). In this series of samples, we obtained a maximum field-effect mobility of $4.4 \times 10^{-2}\,cm^2/Vs$ *in the OFET using 10, 12-heptacosadiynoic acid (HDA). Controlling the substrate temperature from 28 to 70°C, we found the optimum substrate temperature of 40°C for HDA monomer deposition, and obtained a high field-effect hole mobility of* $0.1\,cm^2/Vs$ *in the bottom source-drain electrode configuration.*

Keywords: diacetylene; field-effect mobility; OFET; photopolymerization; substrate temperature

INTRODUCTION

Organic field-effect transistors (OFETs) have rigorously been studied because of their advantageous flexibility and potential use for low-cost device applications such as active matrix circuits in organic light-emitting diodes, electrophoretic displays, and disposable IC tags. However, the field-effect carrier mobility of OFETs is in the order of 10^{-1}–$10^{-5}\,\mathrm{cm^2/Vs}$ in general, and hence this limits practical device applications because of low current density and slow operational speed. In order to enhance field effect mobility, several approaches of forming large crystalline domains and/or improving molecular

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alignment have been introduced [1]. Highly aligned pentacene thin films, in particular, have been reported to have a high field effect mobility of ~1.5 cm^2/Vs [2–6], approaching to that of the organic single crystals. This indicates that the maximum carrier mobility in small molecular thin films is a maximum of ~10 cm^2/Vs as far as molecular interactions are based on the weak van der Waals forces. To overcome this limitation, other long-range π-conjugation systems are anticipated for achieving higher carrier mobility.

Polydiacetylenes are well known as a π-conjugated polymer system with highly controlled packing structure of polymer chains through the photopolymerization of diacetylene monomer crystals. Many researchers investigated the conducting properties of polydiacetylenes, and among them Moses *et al.* reported very high carrier mobility of *ca.* 5 cm^2/Vs determined by the time-of-flight method [7]. On the other hand, Yang *et al.* reported a hole mobility of $\mu_h = 100$ cm^2/Vs calculated from the drift velocity through the J-V characteristics analysis using PTS single crystal (polydiacetylene with toluene-sulfonate side groups) [8], and Hoofman *et al.* reported 1 cm^2/Vs estimated from the microwave conductivity measurement [9]. Our group also reported high field-effect mobility of ~0.8 cm^2/Vs in the OFET device under the morphological control of polydiacetylene film (active layer) [10]. This result shows a significantly higher value than the field-effect mobilities formerly reported such as 1.3×10^{-3} cm^2/Vs [11], 2×10^{-4} cm^2/Vs [12] and 1.5×10^{-5} cm^2/Vs [13] using polydiacetylenes.

In this study, to enhance the field-effect mobility, we tried to control the interchain distance (or packing density of polymer chains) in polydiacetylene thin films by changing the side chain length of diacetylene monomers. We selected five different alkyl chain lengths of diacetylene monocarboxylic acid. An OFET device was prepared by a vacuum deposition of diacetylene monomer, followed by a photopolymerization under Xe-lamp excitation.

EXPERIMENTAL

OFET devices covered with diacetylene monocarboxylic acid as an active layer were prepared in the bottom-contact type configuration as shown in Figure 1. We used five different diacetylene monocarboxylic acids (Fig. 2), that is, we fixed R_2 as $(CH_2)_8COOH$ and changed alkyl chain length of R_1 as 7 (HDDA), 13 (TDA), 15 (PDA), 17 (HAD) and 19 (NDA). The substrate was an n$^+$-Si wafer with 300 nm thick SiO_2 insulating layer, and it was ultrasonically washed with detergent, acetone, and isopropanol, respectively, for 5 min. No additional surface treatment was performed. The bottom-contact type configuration has

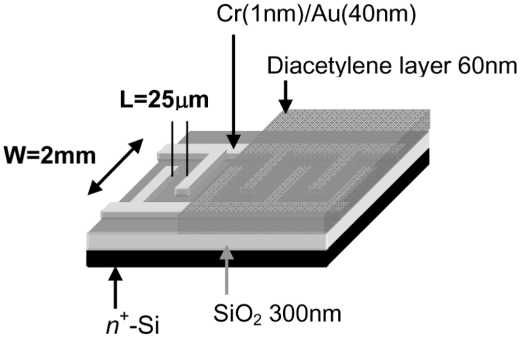
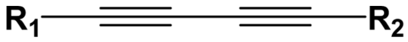


FIGURE 1 Organic FET device structure in the bottom-contact type configuration.

a 60-nm-thick diacetylene monomer layer thermally deposited on Au (40 nm)/Cr (1 nm) comb-type-electrodes, of which channel width is 2 mm and channel length 25 μm. The diacetylene monomer layer was formed using conventional vacuum deposition with the deposition rate of 0.1 nm/s. The diacetylene layer was photopolymerized under Xe-lamp excitation (white light) with the light intensity of 10 mW/cm^2 for 60 min in air. All measurements were carried out in a vacuum of *ca.* 1×10^{-1} Pa at room temperature because the device had unstable TFT



10,12-heptadecadiynoic acid (HDDA)
$R_1=(CH_2)_3CH_3$, $R_2=(CH_2)_8COOH$

10,12-tricosadiynoic acid (TDA)
$R_1=(CH_2)_9CH_3$, $R_2=(CH_2)_8COOH$

10,12-pentacosadiynoic acid (PDA)
$R_1=(CH_2)_{11}CH_3$, $R_2=(CH_2)_8COOH$

10,12-heptacosadiynoic acid (HDA)
$R_1=(CH_2)_{13}CH_3$, $R_2=(CH_2)_8COOH$

10,12-nonacosadiynoic acid (NDA)
$R_1=(CH_2)_{15}CH_3$, $R_2=(CH_2)_8COOH$

FIGURE 2 Molecular structures of diacetylene monomer used in this study.

characteristics in air. The dependence of the drain current (I_d) on the drain voltage (V_d) and the gate voltage (V_g) was measured using a semiconductor parameter analyzer (Agilent 4155).

The highest occupied molecular orbital (HOMO) levels of the metal and the organic layers were measured using an ultraviolet photoelectron spectrometer, AC-1 (Riken Keiki Co.). Also the lowest unoccupied molecular orbital (LUMO) level was estimated by subtracting the band gap energy (E_g) from the HOMO level. Here, the E_g was estimated from the absorption threshold in the UV-visible spectrum.

RESULTS AND DISCUSSION

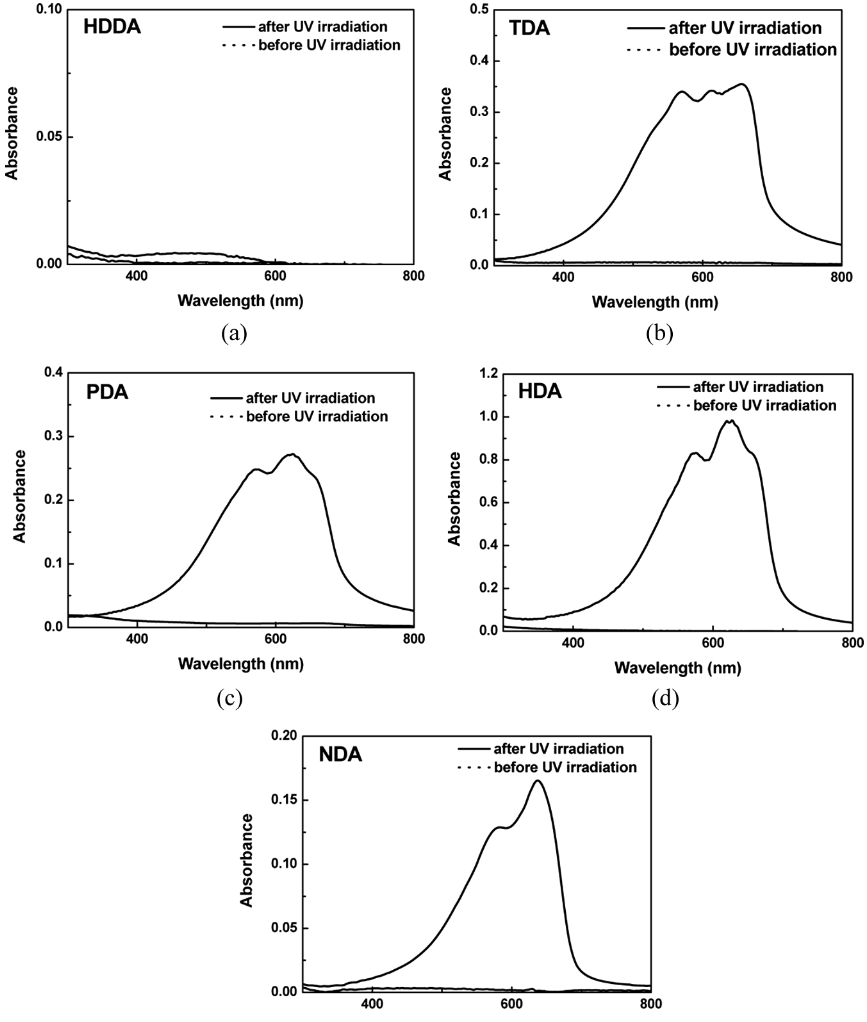
The absorption spectra of deposited diacetylene films before and after the UV-light irradiation are shown in Figure 3. Although no absorption was observed in the visible region before UV-light irradiation, the polymerized films showed blueish golden colors by viewing from the top and/or side angles. Also a strong absorption at λ_{peak} of 600 nm of TDA, PDA, HDA and NDA monomers were observed after the UV-light irradiation, indicating successful polymerization of the diacetylene monomers and hence the extension of π-conjugation of the polydiacetylene main chains. HDDA monomer, however, showed only a small absorption band in the short wavelength side compared to other monomers.

HOMO and LUMO levels of each diacetylene films before and after the UV irradiation are summarized in Table 1, which indicates significant changes of LUMO after UV irradiation. The inset of Figure 4 shows the FET characteristics of HDA device. No FET operation was observed in the device before UV irradiation, but a remarkable change was observed after UV-light irradiation, that is, the HDA device indicated a p-type FET operation due to semiconductor characteristics of extended π-conjugation along the polymerized diacetylene main chain. The field-effect mobility μ [cm^2/Vs] is determined from the slope of the gate voltage V_g *vs* SQRT of drain current I_d (Fig. 4) as

$$\mu = \left(\frac{\sqrt{I_d}}{V_g - V_T}\right)^2 \frac{2L}{WC_i}$$

where L is the channel length [cm], W the channel width [cm], C_i the static capacitance of gate insulator [F/cm^2] and V_T the threshold voltage of channel formation.

The FET characteristics of the polydiacetylene thin film devices were summarized in Table 2. In this series of samples, we obtained a



(a) (b)

(c) (d)

(e)

FIGURE 3 UV-Vis absorption spectra of diacetylene deposited film before and after UV-light irradiation. (a) HDDA, (b) TDA, (c) PDA, (d) HDA, (e) NDA.

maximum field-effect mobility of $4.4 \times 10^{-2}\,\mathrm{cm^2/Vs}$ in the OFET using HDA. It should be noted that the photo- polymerization of diacetylene greatly depends on the packing distance of conjugated main chains (5Å) [14]. Therefore, HDA may have an optimum packing distance with suitable length of side chain. The HDDA did not show FET operation

TABLE 1 Energy Diagram of Diacetylene Films Before and After UV-Light Irradiation. (HOMO and LUMO Levels in eV)

	HDDA	TDA	PDA	HAD	NDA
Before UV irradiation (HOMO/LUMO)	5.3/1.1	5.2/1.2	5.3/1.2	5.3/1.4	5.7/1.4
After UV irradiation (HOMO/LUMO)	5.5/3.5	5.2/3.5	5.2/3.5	5.3/3.5	5.3/3.5

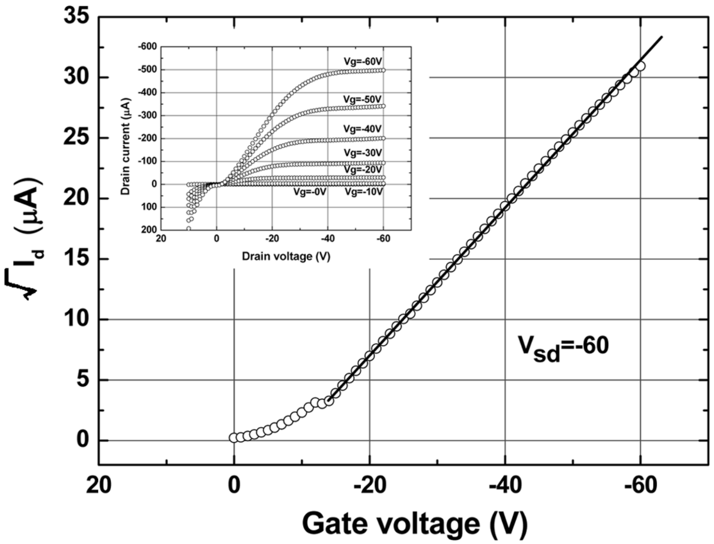


FIGURE 4 I_d–V_d and I_d–V_g characteristics of HDA device after UV-light irradiation. (I_d is the drain current, V_d the drain voltage, and V_g the gate voltage.)

TABLE 2 Field-Effect Mobility of Different Diacetylene Monomers

	Mobility (cm^2/Vs)	V_T (V)
HDDA	—	—
TDA	2.4×10^{-2}	–5.0
PDA	3.0×10^{-2}	–6.2
HDA	4.4×10^{-2}	–3.2
NDA	1.0×10^{-3}	–4.0

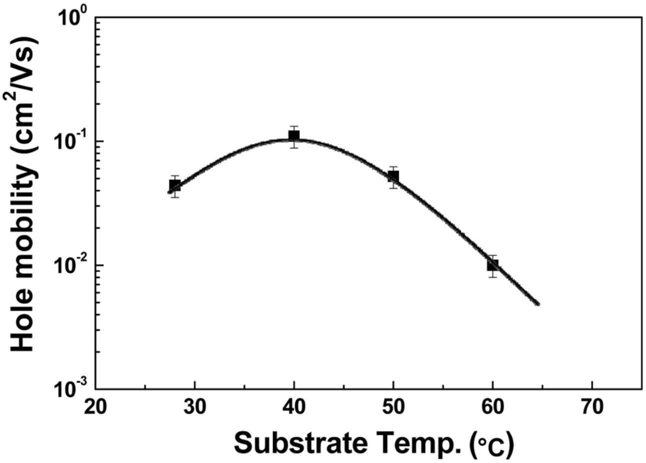
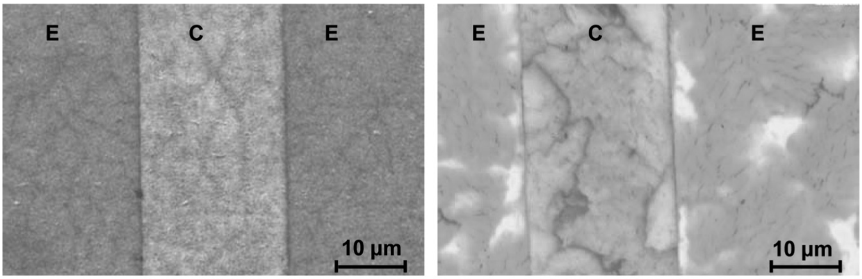


FIGURE 5 Substrate temperature dependence of hole mobility in bottom-contact type device using HDA.

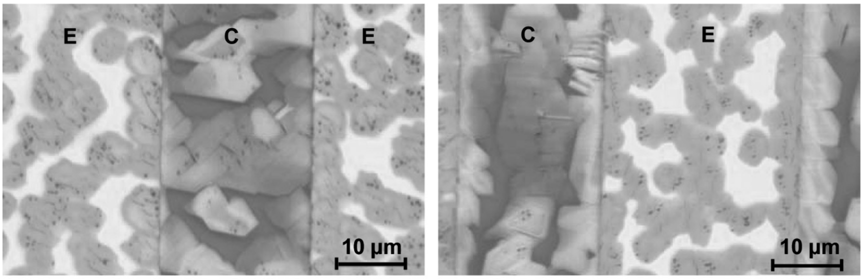
both before and after UV-light irradiation. This is clearly explained by the optical absorption spectrum which shows the poor extension of π-conjugation even after the photopolymerization.

Furthermore, we successfully improved the FET characteristics by changing the substrate temperature during the deposition of HDA monomers. We changed the substrate temperature from 28 to 70°C during the deposition of HDA-monomer layer and the photopolymerization of HDA layer. Figure 5 shows the substrate temperature dependence of μ_h in the bottom contact type configuration. A maximum μ_h of $0.1\,cm^2/Vs$ was obtained at an optimum temperature of 40°C. Furthermore, a rapid decrease of μ_h was observed at substrate temperatures higher than 40°C, and no FET operation at substrate temperature 70°C.

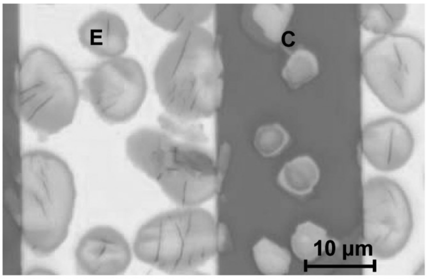
We investigated the surface morphologies of the polydiacetylene films at each temperature by optical microscope (Fig. 6). At a temperature of $T = 28°C$, the photopolymerized HDA films showed smooth but a number of small crystallites. At $T = 40°C$ the small crystallites disappeared and a continuous crystalline texture covered the channel surface. At $T = 50°C$, the film surface had continuous crystalline domains, however, the size of vacancy increased greatly, which suggests the thickening of the crystalline domains. At $T = 60°C$, this tendency was developed further and the contact of crystalline domains were lost. At substrate temperatures of 70°C the isolated island structure of diacetylene domains appeared and this resulted in an inadequate coverage of the underlying insulator layer. The appearance of



(a) **T=28°C** (b) **T=40°C**



(c) **T=50°C** (d) **T=60°C**



(e) **T=70°C**

FIGURE 6 Optical microscope images of polydiacetylene thin film (HDA) formed at various substrate temperatures of 28, 40, 50, 60, and 70°C. (Scale bar is 10 μm, E: electrode, C: channel)

these island structures could be due to the re-evaporation of HDA monomers during the HDA film formation.

CONCLUSION

In summary, we observed typical p-type FET characteristics in photopolymerized polydiacetylene thin film (HDA) with a maximum

μ_h of $4.4 \times 10^{-2}\,\text{cm}^2/\text{Vs}$ in the bottom-contact type device. The results suggested the optimum packing of diacetylene monomers and π-conjugated polymer main chain formation after photopolymerization. Furthermore, the field-effect mobility in a HDA–polydiacetylene film was significantly enhanced by controlling the substrate temperature. The highest μ_h obtained was $0.1\,\text{cm}^2/\text{Vs}$ at the substrate temperature of $T = 40°\text{C}$. From the optical microscope observations it was suggested that the formation of continuous large domains in the polydiacetylene layer was a key to obtaining a high μ_h. The formation of isolated island structure in the polydiacetylene layer reduces greatly the FET characteristics.

We will work on the different device structure, that is, the top contact type configuration of OFET in future following our former evidence of PDA monomer devices.

REFERENCES

[1] Sirringhaus, H., Wilson, R. J., Friend, R. H., Inbasekaran, M., Wu, W., Woo, E. P., Grell, M., & Bradley, D. D. C. (2000). *Appl. Phys. Lett.*, *77*, 406.

[2] Laquindanum, J. G., Katz, H. E., Lovinger, A. J., & Dodabalapur, A. (1996). *Chem. Mater.*, *8*, 2542.

[3] Klauk, H., Gundlach, D. J., Nichols, J. A., & Jackson, T. N. (1999). *IEEE Trans. Electron Devices.*, *46*, 1258.

[4] Nelson, S. F., Lin, Y.-Y., Gundlach, D. J., & Jackson, T. N. (1998). *Appl. Phys. Lett.*, *72*, 1854.

[5] Choo, M. H., Kim, J. H., & Im, S. (2002). *Appl. Phys. Lett.*, *81*, 4640.

[6] Sekitani, T., Iba, S., Kato, Y., & Someya, T. (2004). *Appl. Phys. Lett.*, *85*, 3902.

[7] Mosesand, D. & Heeger, A. J. (1989). *J. Phys.: Condens. Matter.*, *1*, 7395.

[8] Yang, Y., Lee, J. Y., Miller, P., Li, L., Kumar, J., & Tripathy, S. K. (1991). *Solid State Comm.*, *77*, 763.

[9] Hootman, R. J. O. M., Siebbeles, L. D. A., de Haas, M. P., Hummel, A., & Bloor, D. (1998). *J. Chem. Phys.*, *109*, 1885.

[10] Nishide, J., Oyamada, T., Akiyama, S., Sasabe, H., & Adachi, C. (2006). *Adv. Mater.*, *18*, 3120.

[11] Koyanagi, T., Muratsubaki, M., Hosoi, Y., Shibata, T., Tsutsui, K., Wada, Y., & Furukawa, Y. (2006). *Chem. Lett.*, *35*, 20.

[12] Lee, J. Y., Aleshin, A. N., Kim, D. W., Lee, H. J., Kim, Y. S., Wegner, G., Enkelmann, V., Roth, S., & Park, Y. W. (2005). *Synth. Met.*, *152*, 169.

[13] Zou, G., Lim, E., Kajimoto, N., Kohn, H., Ohshima, Y., Manaka, T., & Iwamoto, M. (2007). *Jpn. J. Appl. Phys.*, *46*, 3071.

[14] Matsumoto, A., Sada, K., Tashiro, K., Miyata, M., Tsubouchi, T., Tanaka, T., Odani, T., Nagahama, S., Tanaka, T., Inoue, K., Saragai, S., & Nakamoto, S. (2002). *Angew. Chem. Int. Ed.*, *41*, 2502.