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Circular dichroism and electroluminescence of poly(diacetylene) film with chirality*

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By applying only circularly polarized light (CPL) irradiation to evaporated achiral diacetylene (DA) monomer film during its photopolymerization process, we prepared poly(diacetylene) (PDA) films that show circular dichroism (CD). The left- or right-handed chirality was induced in the polymerized PDA films by the left- and right-CPL irradiation. We studied physical properties of the prepared PDA films, including their electrical and optical properties. The induced chirality in PDA films was not destroyed after annealing at 353 K for 10 min, whilst their blue-phase was changed into a red one. The intensity of the CD signal was dependent on the substrate temperature employed for the monomer deposition. Electroluminescence was found to be enhanced with the polymerized PDA films installed as an active layer of organic field-effect transistors.

Key words: *poly(diacetylene); circularly polarized light; chirality; electroluminescence*

1. Introduction

Recently, chiral conjugated polymer with helical structure has drawn attention in electronics, e.g., as a source material of inductor, as an active layer of polarized luminescence devices, etc., and a variety of preparation techniques have been proposed [1]. Among them, the most well-known preparation method is to use a chiral dopant. Akagi et al. prepared helical polyacetylene (PA) from acetylene monomers mixed with chiral liquid crystal [2, 3]. A method without using dopant has also been proposed. Wu et al. introduced chirality into an achiral liquid crystal polymer by using a conformational change of azobenzene by photoisomerization [4]. However, so prepared conjugated polymers contain impurities of a chiral dopant or photofunctional

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moiety used in their fabrication. We found a way, without using chiral dopant or photofunctional moiety, for the fabrication of pure chiral poly(diacetylene) (PDA) films by only applying circularly polarized light (CPL) to precursor achiral diacetylene (DA) monomer film in its photopolymerization process [5]. By the use of this technique, we could prepare chiral PDA Langmuir–Blodgett (LB) films as well as chiral PDA evaporated films. However, the details of the induced chirality are still not clear. It is necessary to understand the relationship between the induced chirality and the conditions under which films are prepared, e.g. annealing temperature, irradiation time of CPL, etc. Furthermore, we have not yet studied the physical properties of the prepared chiral PDA films, e.g., their electrical transport property. In this paper, we study the induced chirality in PDA films prepared at various substrate temperatures, and then investigate the electrical transport property and electroluminescence (EL) of the prepared PDA films that were installed as an active layer of organic field-effect transistor (FET) with gate-SiO_2 insulator.

2. Sample preparation

10,12-Tricosadiynoic acid (TDA), $CH_3(CH2)_9C{\equiv}C{-}C{\equiv}C(CH_2)_8COOH$, was purchased from Tokyo Chemical Industry Co., Ltd., and used without further purification. The TDA monomers were deposited on a glass substrate by the vacuum evaporation. The evaporation rate was set to 0.8 Å/s, and the film thickness of deposited TDA was approximately 100 nm. The pressure was lower than 2.3×10^{-4} Pa during deposition, and the substrate temperature was 313 K. After the TDA deposition, the substrate temperature was kept at 293 K, and the substrate was immediately removed from the vacuum system for photoirradiation. Photopolymerization of TDA films was carried out using 314 nm UV light from a high-pressure Hg lamp (Hamamatsu L-8333), where the UV light was irradiated onto the samples perpendicularly.

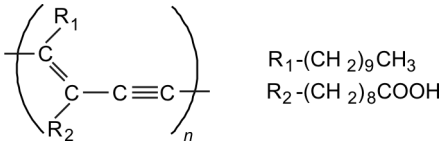

Fig. 1. Chemical structure of PDA

The intensity of each left- and right-CPL was approximately 19.4 mW/cm^2, and the irradiation time was 25 min. After photoirradiation, blue-phase PDA was polymerized from TDA monomers (Fig. 1). Finally, red-phase PDAs were prepared by annealing (353 K, 10 min). For the study of the carrier transport property, chiral red-phase PDA films polymerized using left- and right-CPL were prepared on the SiO_2 (500 nm)/n-Si substrate, and it was installed as an active layer of the bottom contact FET (Fig. 2). EL was measured using the FET under alternating current (ac) voltage.

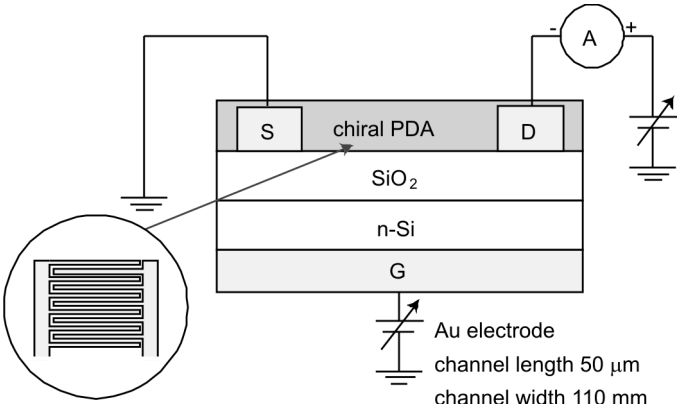

Fig. 2. Measurement set up for the chiral red phase PDA-FET (bottom contact type)

3. Results and discussion

3.1. Chiral PDA and optical properties

The circular dichroism (CD) spectra of red-phase PDAs polymerized by left- and right-CPL are shown in Fig. 3 (for the CD measurement, the spot area of incident light was 7×7 mm^2).

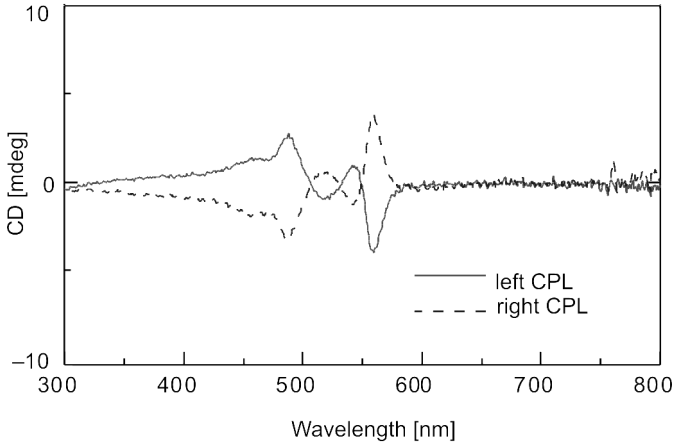

Fig. 3. CD spectra of evaporated PDA films. The samples were fabricated at 313 K. Solid and dashed lines represent the spectra for the films polymerized with left (solid line) and right (dashed line) CPL irradiation

In our previous study, achiral TDA monomers were deposited by evaporation on the glass substrate, and then transformed into chiral blue-phase PDA by irradiating

CPL. The induced chirality withstood for a long time after the phase transition from blue-phase to a red one [5]. It was considered that the phase transition of PDA was caused by the distortion of the backbone [6], that is, single-bond of the backbone rotated in accordance with the reorientation of the side chains during annealing. On the other hand, the surface morphology was strongly dependent on the substrate temperature employed for the evaporation. Tanaka et al. reported that crystallinity of an *n*-paraffin film changed with respect to the substrate temperature [7]. The vacuum-deposited TDA film is composed of a large number of domains, and each domain consists of the rod-like TDA monomers resembling an *n*-paraffin chain. Polymerization of TDA monomers proceeds on keeping the original crystal structure (i.e., topochemical reaction) [8, 9]. Therefore, a large conjugated system is formed perpendicularly to the long axis of monomers, and crystallinity of PDA film prepared by UV light irradiation can change, depending on the packing structure. Furthermore, when CPL irradiation was introduced into the polymerization process after controlling the substrate temperature, a stronger CD signal was observed, accompanied by larger domains on the surface at high substrate temperature (313 K) [10, 11].

3.2. Electrical transport property of chiral PDA

Figure 4 shows typical current–voltage (I_{DS}–V_{DS}) characteristics of chiral PDA -FET at various gate voltages V_G (from 0 to ca. –100 V), measured under the pressure lower than 1×10^{-4} Pa. As shown in the figure, I_{DS} increased when a negative gate voltage was applied, and p-channel type FET behaviour was confirmed.

In contrast, no n-channel FET behaviour was observed when a positive gate voltage was applied. Under the gradual channel approximation, I_{DS} in a saturated region is expressed as

$$I_{DS} = \frac{1}{2}\frac{W}{L}\mu C_{OX}\left(V_G - V_{Th}\right)^2 \tag{3.1}$$

where L and W are the channel length and width, respectively, and C_{OX} is the capacitance per unit area of the SiO_2 gate insulator [12]. Mobility (μ) of left- and right-handed chiral PDAs was nearly the same ($\approx10^{-6}$ cm^2/V·sec: V_{DS} = –60 V). p-Channel behaviour was also reported using bottom and top contact type FET with blue-phase PDA, polymerized by unpolarized light [13, 14], where I_{DS} saturated. For chiral red-phase PDA, I_{DS} reached a maximum, and then decreased with the increase in V_{DS}. Similar behaviour was observed for top contact FET with chiral blue-phase PDA polymerized by CPL. Carrier trapping during the device operation presumably was responsible for such *I*–*V* characteristics [15]. Detailed experiments and analysis are now proceeding to reveal the origin of the observed behaviour. It should be noted that no clear difference between left- and right-CPL was recorded in the *I*–*V* characteristics, and the results showed good reproducibility.

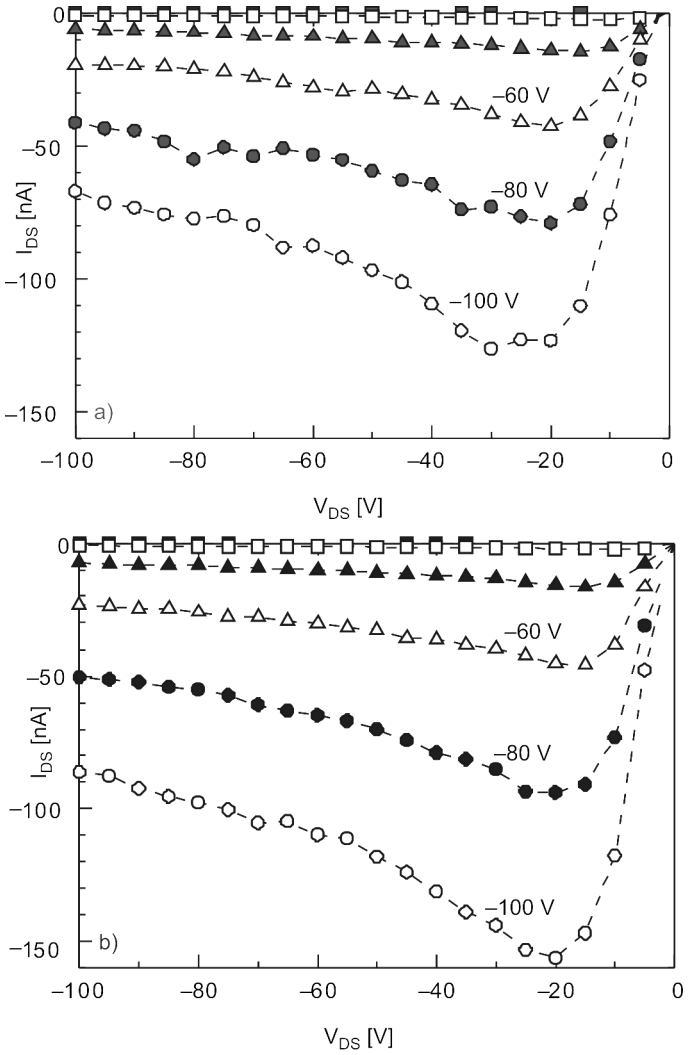

Fig. 4. Typical I_{DS}-V_{DS} characteristics of chiral red-phase PDA-FET. The films were polymerized by using left- (a) and right-CPL (b) irradiation, respectively

These results are reasonable, because the chirality of molecules has no influence on the electrical characteristics of the direct current (dc) e.g., *I–V* characteristics.

3.3. Electroluminescence for chiral PDA

The possibility of EL enhancement from chiral PDA was investigated. There are many papers about EL using organic materials [16]. To observe EL from organic materials effectively under an applied dc current, the relationship between the HOMO and the LUMO gap of organic material and the work function of the metal electrode

should be known. Nevertheless, our group reported EL enhanced from tetracene–FET with Au electrode under an applied ac voltage. That EL was caused by alternating injection of hole and electron from the same electrode [17, 18]. In this paper, EL from the bottom contact type FET structure was investigated under the pressure lower than 1×10^{-4} Pa, where source and drain electrodes were connected to each other and a square wave was applied (frequency 50 kHz).

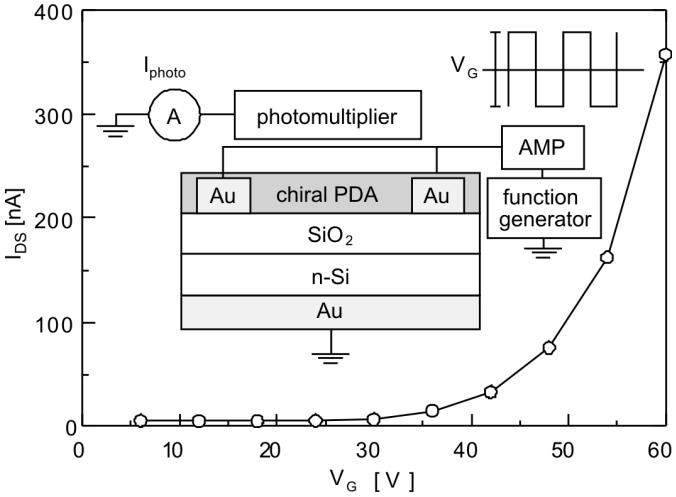

Fig. 5. ac voltage (V_G) dependence of EL intensity from chiral red-phase PDA-FET

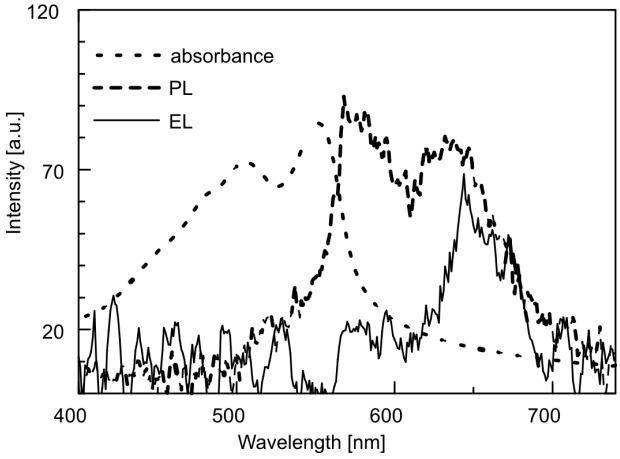

Fig. 6. Absorption and luminescence spectra of chiral red-phase PDA film.
ac amplitude and measuring pressure are 120 $V_{p\text{-}p}$ and ambient atmosphere, respectively

Figure 5 shows the V_G dependence of the EL intensity (recorded as photocurrent using the photomultiplier tube) from the chiral red-phase PDA-FET. The increase in the EL intensity was observed upon applying V_G in chiral red-phase PDAs, polymer-

ized by left- and right-CPL, respectively. For the measurement, the detector was a photomultiplier tube (Hamamatsu R-3896), capable of detecting extremely weak signals in the visible region. As shown in Fig. 6, the EL signal was observed at a longer wavelength of the absorption band of red-phase PDA, and the peak position of the EL spectrum was coincident with that of photoluminescence (PL). Accordingly, EL from chiral PDA was observed. In the past, EL enhanced from red-phase PDA, sandwiched between ITO and Al electrodes, was reported [19]. However, to the best of the author's knowledge, there has been no report concerning EL using FET under an ac voltage. These results obtained in the present paper testify to the novel functionality of the chiral PDA.

4. Conclusion

The strength of induced chirality of PDA was dependent on the substrate temperature. Substrate temperature was set to 313 K during the evaporation process, and both chiral blue-phase PDAs, polymerized by left- and right-CPL, were prepared on the glass substrate. The prepared blue-phase PDAs were annealed and changed into the chiral red-phase PDAs which showed good stability. In the same way, chiral red -phase PDA was prepared on the SiO_2 substrate as an active layer of contact type FET. In the *I–V* measurement, both chiral red-phase PDA-FETs showed p-channel behaviour. On the other hand, in the study of EL, an increase in the current was recorded, under the applied ac voltage, by using a photomultiplier.

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References

[1] YASHIMA E., MAEDA K., OKAMOTO Y., Nature, 399 (1999), 449.
[2] AKAGI K., PIAO G., KANEKO S., HIGUCHI I., SHIRAKAWA H., KYOTANI M., Synth. Met., 102 (1999), 1406.
[3] AKAGI K., GUO S., MORI T., GOH M., PIAO G., KYOTANI M., J. Am. Chem. Soc., 127 (2005), 14647.
[4] WU Y., NATANSOHN A., ROCHON P., Macromolecules, 37 (2004), 6801.
[5] MANAKA T., KON H., OHSHIMA Y., ZOU G., IWAMOTO M., Chem. Lett., 35 (2006), 1028.
[6] LEE D. C., SAHOO S. K., CHOLLI A. L., SANDMAN D. J., Macromolecules, 35 (2002), 4347.
[7] TANAKA K., OKUI N., SAKAI T., Thin Solid Films, 196 (1991), 137.
[8] ENKELMANN V., WEGNER G., Angew. Chem., Int. Ed. Engl., 16 (1977), 416.
[9] ENKELMANN V., *Structural Aspects of the Topochemical Polymerization of Diacetylenes*, [in:] H. J. Cantow (Eds.), *Advances in Polymer Science*, Vol. 63, Springer, Berlin, 1984, p. 91.
[10] KOHN H., OHSHIMA Y., MANAKA T., IWAMOTO M., Jpn. J. Appl. Phys., 47 (2008), 1359.
[11] KOHN H., OHSHIMA Y., MANAKA T., IWAMOTO M., Macromol. Symp., 268 (2008), 77.

[12] SZE S. M., *Physics of Semiconductor Devices*, John Wiley & Sons, New York, 1981.
[13] KOYANAGI T., MURATSUBAKI M., HOSOI Y., SHIBATA T., TSUTSUI K., WADA Y., FURUKAWA Y., Chem. Lett., 35 (2006), 20.
[14] ZOU G., LIM E., KAJIMOTO N., KOHN H., OHSHIMA Y., MANAKA T., IWAMOTO M., Jpn. J. Appl. Phys., 46 (2007), 3071.
[15] LINDNER TH., PAASCH G., SCHEINERT S., J. Appl. Phys., 98 (2005), 114505.
[16] ZAUMSEIL J., FRIEND R. H., SIRRINGHAUS H., Nat. Mater., 5 (2006), 69.
[17] OHSHIMA Y., KOHN H., LIM E., MANAKA T., IWAMOTO M., Jpn. J. Appl. Phys., 47 (2008), 1297.
[18] OHSHIMA Y., KOHN H., LIM E., MANAKA T., IWAMOTO M., Jpn. J. Appl. Phys., 47 (2008), 3200.
[19] GIORGETTI E., SOTTINI S., DEL ROSSO T., MARGHERI G., ALLOISIO M., DELLEPIANE G., Synth. Met., 147 (2004), 271.

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