Extended Abstracts of the 2009 International Conference on Solid State Devices and Materials, Sendai, 2009, pp1166-1167

Liquid Phase Crystal Growth of an Alternating Co-Oligomer Composed of Thiophene and Phenylene Rings

Takeshi Yamao[1], Yoshihiro Nishimoto[1], Hiroshi Akagami[1], Toshifumi Katagiri[1,2] and Shu Hotta[1]

[1]Kyoto Institute of Technology, Department of Macromolecular Science and Engineering,
Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan.
Phone: +81–75–724–7780 E-mail: yamao@kit.ac.jp
[2] Sumitomo Seika Chemicals Co., Ltd., Befu Technical Office, Befu Works,
346-1 Miyanishi, Harima-cho, Kako-Gun, Hyogo 675-0145, Japan.

1. Introduction

Organic crystals comprising π-conjugated molecules are promising as functional materials. The peculiar physical properties e.g. high carrier mobilities in organic field-effect transistors (OFETs) [1], spectrally narrowed emissions [2] and laser oscillations [3] have been observed in these crystals. The regular arrangement of the molecules is responsible for them. It will, therefore, be important for device applications to make the most use of organic crystals with highly aligned molecules. Of these materials, thiophene/phenylene co-oligomers (TPCOs) [4,5] are particularly promising.

The TPCOs include several compounds in which thiophene and phenylene rings assume an alternating arrangement. The crystals of such compounds exhibit moderately high carrier mobility [6,7] and unique optical properties e.g. high quantum efficiency of emission greater than 0.7 [8]. A typical example is AC5; see Fig. 1(a). In the present studies we investigate the charge transport of another alternating oligomer AC'7 [Fig. 1(b)] of higher molecular-weight version [9].

Meanwhile, we have been successful in developing the method of growing organic single crystals of high quality in a liquid phase [10]. This enables us to produce them directly onto the substrates. Thus the grown crystals are readily applicable to the device fabrication. We now apply this method to making the single crystals of AC'7 so that the charge transport characteristics can be studied on an OFET device.

2. Experimental

The method for the synthesis and purification of AC'7 is described in the literature [9]. The detailed procedure and apparatus for the crystal growth can be seen elsewhere [10]. We used a 1,2,4-trichlorobenzene suspension (20 ml) of AC'7 (5–8 mg). We obtained the crystals on SiO_2/Si substrate after the suspension was kept at 190 °C for 24–148 h.

The top-contact OFETs were fabricated by vacuum deposition of Au source and drain contacts on the grown crystals. The Si was used as the gate contact, and SiO_2 layer was used for the gate insulator. The electrical characteristics were measured in the dark both under an ambient environment and under vacuum ($<5\times10^{-3}$ Pa). The carrier mobilities of the OFETs were estimated from the electrical data in the saturation region [11].

3. Results and Discussion

Polarizing micrographs of a grown AC'7 crystal are shown in Fig. 2. These were taken under the extinction position [Fig. 2(a)] and the diagonal position [Fig. 2(b)] of the crossed Nicols. The microscope observations clearly indicate that the AC'7 crystal is a hexagon [Fig. 2(b)]. The fact that the crystal entirely vanishes at the extinction position [Fig. 2(a)] illustrates that it is a single crystal.

We measured the X-ray diffraction patterns of AC'7 on the substrate. Figure 3(a) shows the result for the grown AC'7 crystals in comparison with that for the as-synthesized powder spread over the substrate [Fig. 3(b)]. In the single crystals, only the first- and higher-order peaks (up to 19th) from the same diffraction plane are observed [Fig. 3(a)]. The plane distance evaluated from the peaks is d = 29.70 Å. This value is in agreement with the AC'7 molecular length (29.23 Å) estimated from a geometrically optimized molecular structure using PM3 [12] in a MOPAC2002 program [13]. As for the as-synthesized material, on the other hand, we observed peaks occurring from planes other than that associated with the molecular length [denoted with asterisks in Fig. 3(b)]. The results of the polarizing micrograph and the diffraction pattern obviously

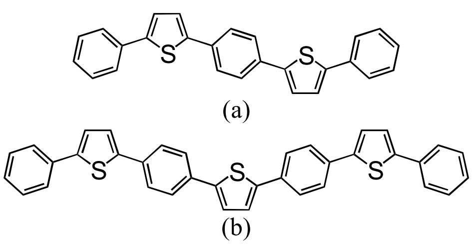

Fig. 1 Structural formulae of (a) AC5 and (b) AC'7.

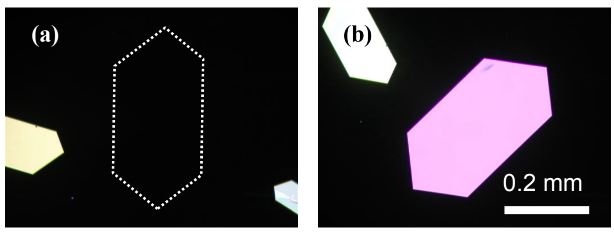

Fig. 2 Polarizing micrographs of an AC'7 crystal. These are taken under (a) the extinction position and (b) the diagonal position of the crossed Nicols. The white dotted line is a guide to eye.

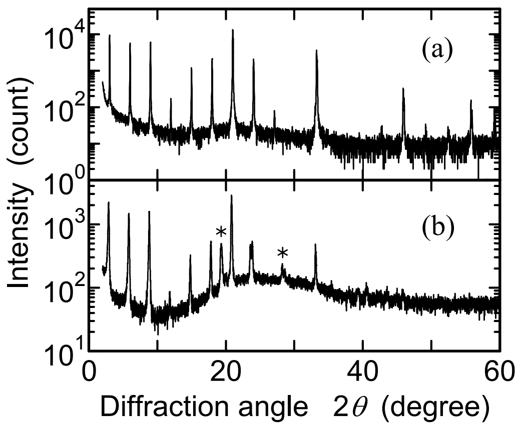

Fig. 3 X-ray diffraction patterns of (a) AC'7 crystals and (b) as-synthesized powder.

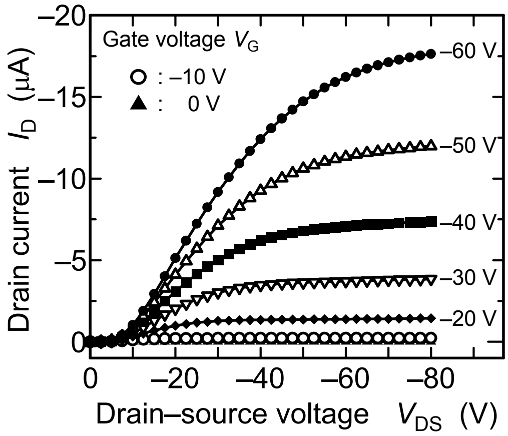

Fig. 4 Output characteristics of the AC'7 crystal OFET fabricated on the SiO_2/Si substrate.

indicate that the AC'7 crystal consists of the regular molecular layered structure as in the case of AC5 crystal [14].

Figure 4 shows the output characteristics of the OFET made of an AC'7 crystal on an SiO_2/Si substrate. The diagram depicts the result measured in vacuum. The drain currents increase around the drain-source voltage of –10 V. The presence of the convex-downward behavior of the drain currents near the origin is indicative of the somewhat poor electrical connection (non-ohmic contact) between the AC'7 crystal and the Au electrodes.

The mobility and threshold voltage were estimated to be 0.098 cm^2/Vs and –3.4 V, respectively. Those measured in air were 0.090 cm^2/Vs and 0.42 V. These mobilities are larger than those obtained for the AC5 crystal OFETs; the mobility of the OFET made of a vapor-phase-grown AC5 crystal was 0.021 cm^2/Vs (with SiO_2 used for the gate insulator) [7] and that in the liquid phase was 0.022 cm^2/Vs (with a polymer used for the gate insulator) [6]. The larger mobility can be attributed to longer π-conjugation of AC'7 than that of AC5.

4. Conclusions

We have grown the single crystals of AC'7 directly on the SiO_2/Si substrates in the liquid phase. The grown crystals are well-defined hexagon and composed of the regular molecular layered structure. The top-contact OFETs made of these crystals show the mobility of ~0.1 cm^2/Vs. This number was higher than that obtained for AC5. The present results show that the AC'7 crystals are potentially useful for the electrical device applications.

Acknowledgements

This work was supported by Grant-in-Aid for Science Research in a Priority Area “Super-Hierarchical Structures” (Grant No. 17067009) and by Grant-in-Aid for Exploratory Research (Grant No. 20655041) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

References

[1] J. Takeya, M. Yamagishi, Y. Tominari, R. Hirahara, Y. Nakazawa, T. Nishikawa, T. Kawase, T. Shimoda, S. Ogawa, Appl. Phys. Lett. **90** (2007) 102120.

[2] M. Nagawa, R. Hibino, S. Hotta, H. Yanagi, M. Ichikawa, T. Koyama, Y. Taniguchi, Appl. Phys. Lett. **80** (2002) 544.

[3] M. Ichikawa, R. Hibino, M. Inoue, T. Haritani, S. Hotta, K. Araki, T. Koyama, Y. Taniguchi, Adv. Mater. **17** (2005) 2073.

[4] S. Hotta, S. A. Lee, T. Tamaki, J. Heterocyclic Chem. **37** (2000) 25.

[5] S. Hotta, H. Kimura, S. A. Lee, T. Tamaki, J. Heterocyclic Chem. **37** (2000) 281.

[6] T. Yamao, H. Kuriki, T. Miki, S. Hotta, J. Nanosci. Nanotechnol. **9** (2009) 165.

[7] T. Yamao, S. Ota, T. Miki, S. Hotta, R. Azumi, Thin Solid Films **516** (2008) 2527.

[8] S. A. Lee, S. Hotta, F. Nakanishi, J. Phys. Chem. A **104** (2000) 1827.

[9] S. Hotta, T. Katagiri, J. Heterocyclic Chem. **40** (2003) 845.

[10] T. Yamao, T. Miki, H. Akagami, Y. Nishimoto, S. Ota, S. Hotta, Chem. Mater. **19** (2007) 3748.

[11] S. M. Sze, *Physics of Semiconductor Devices*, John Wiley & Sons, Inc., New York, (1981).

[12] J. J. P. Stewart, J. Comput. Chem. **10** (1989) 209.

[13] J. J. P. Stewart, MOPAC2002 (version 1.5) (Fujitsu Ltd., Tokyo, 2003).

[14] T. Yamao, Y. Taniguchi, K. Yamamoto, T. Miki, S. Ota, S. Hotta, M. Goto, R. Azumi, Jpn. J. Appl. Phys. **46** (2007) 7478.