



Structural analysis of benzothienobenzothiophene-based soluble organic semiconducting crystals grown by liquid crystal solvent



Yosei Shibata*, Tomoya Matsuzaki, Takahiro Ishinabe, Hideo Fujikake

Department of Electronic Engineering, Graduate School of Engineering, Tohoku University, Sendai 980-8579, Japan

ARTICLE INFO

Article history:

Received 23 January 2018

Received in revised form 16 April 2018

Accepted 17 April 2018

Available online 18 April 2018

Communicated by Keshra Sangwal

Keywords:

A1. Solvent

A1. X-ray diffraction

A2. Single crystal growth

B1. Organic compounds

B2. Semiconducting materials

ABSTRACT

In this study, we analyzed organic semiconducting single crystals composed of benzothienobenzothiophene derivatives (2,7-dioctyl[1]benzothieno[3,2-b][1]benzothiophene, C₈-BTBT) grown by nematic-phase liquid crystal (LC) solvent. As a result, we clarified that the crystal *b*-axis direction of the C₈-BTBT single crystals was consistent with the LC alignment direction. By optical evaluation and simulation based on density functional theory, we found that the C₈-BTBT single crystals in LC solvent exhibited a novel molecular conformation having alkyl chains oriented toward the *b*-axis.

© 2018 Elsevier B.V. All rights reserved.

1. Introduction

Solution-processed single crystal growth of organic semiconductor materials has attracted much interest not only for scientific reasons, but also for printable electronic devices, such as organic field-effect transistors, because application to the printing process has the potential to yield low cost and large-area device production. Organic transistors are necessary for flexible electronic devices, such as flexible displays, RF-ID tags, and sensor devices. The reliability of organic semiconducting devices is one of the most critical factors for application of the integrated circuit, such as the pixel driving circuit for electronic displays. The crystallinity and molecular orientation of organic semiconducting crystals affects carrier mobility [1,2]. For this reason, it has become necessary to achieve solution-processing structural control of organic semiconducting crystals for printable devices.

To date, several advanced solution processes have been studied. These include double-shot inkjet printing [3], edge-casting [4], solution shearing [2,5], and off-center spin coating methods [6]. In these solution processes, the layered-crystalline organic semiconductor, 2,7-dioctyl[1]benzothieno[3,2-b][1]benzothiophene (C₈-BTBT), a renowned *p*-type semiconductor [7], has been used due to its excellent air stability and mobility comparable to amorphous silicon transistors. Additionally, structural studies of

C₈-BTBT single crystals have been conducted to examine the reasons for their high-performance characteristics [8]. The C₈-BTBT crystal has a herringbone packing structure due to its alkyl chains and anisotropy of intermolecular interaction [9]. To ensure the reliability and high performance of organic semiconducting devices using benzothienobenzothiophene derivatives, directional control of C₈-BTBT single crystals toward electrodes is required because the overlapping of π -orbitals among molecules is one of the most important characteristics for optimization of mobility. However, the solution process technology required to fulfill both the formation of single crystals and the directional control of their crystalline axes has not been fully established.

For development of a directional control technique for C₈-BTBT single crystals, we focused on a solution-processed crystal growth method using a nematic-phase liquid crystal (LC) as a solvent. The intermolecular interaction between organic semiconducting molecules and LC molecules has the potential for free directional control of organic semiconducting crystals because the molecular alignment state of LC can be determined by the use of polyimide films and an electrical field. Previously, we reported that the optimization of LC layer thickness and C₈-BTBT concentration enables single crystalline growth in homogeneously aligned nematic-phase LC solvent (4-cyano-4'-pentylbiphenyl, 5CB) injected into a rubbing-treated LC cell structure [10]. In this work, we discussed the single crystalline growth condition of C₈-BTBT in terms of the amount of solute supplied to the crystal nucleus. To evaluate the controllability of crystal direction in the LC-assisted C₈-BTBT, we investigated

* Corresponding author.

E-mail address: y.shibata@ecei.tohoku.ac.jp (Y. Shibata).

the effect of alignment distribution by lateral electric field on the crystal growth of C₈-BTBT [11]. From these studies, we have so far clarified that the direction of one crystal axis in single crystalline C₈-BTBT is controlled by the LC solvent, because the optic axis of the C₈-BTBT single crystal was parallel to the alignment direction of 5CB molecules. However, the growth mechanism of the uniaxially oriented C₈-BTBT single crystals in 5CB solvent remained unclear. Elucidation of the crystal growth mechanism using LC solvent will lead to high-performance and reliable integrated electrical circuits using organic transistors.

Here, we report a structural analysis of C₈-BTBT single crystals obtained using parallel-aligned LC solvent based on density functional theory (DFT). In this paper, on the basis of an optical evaluation, we also discuss the crystal growth process of C₈-BTBT single crystals in parallel-aligned LC solvent.

2. Experimental

The procedure for C₈-BTBT crystal growth using LC solvent is presented in Fig. 1(a). The polyimide films (AL1254, purchased from JSR Corp.) were spin-coated at 3000 rpm for 30 s on an ultrasonically cleaned glass substrate. Then, the polyimide films were baked at 200 °C for 1 h. Next, a rubbing treatment was carried out on the polyimide films using a rubbing system (RM-50; EHC Corp.), as shown in Fig. 1(a)–I. The rubbing condition was as follows: the rotation rate of the roller was 500 rpm, and its diameter was 4.5 cm, the substrate carrier speed was ca. 3 mm/s, and the push length of rubbing cloth to the substrate was ca. 0.1 mm. We constructed the parallel-aligned LC cell structure (opposite rubbing directions between top and bottom substrates) using rubbing-treated two-glass/polyimide substrates. Prior to crystal growth, we confirmed that only nematic-phase LC molecules exhibited parallel alignment in such cells. Here, we define parallel alignment of LC as the parallel state between molecular long axis and rubbing direction. The solution composed of C₈-BTBT and 5CB solvent was injected into the LC cells on a hotplate at 60 °C. Compared with solvent effect of 5CB, the solution with toluene solvent was injected into the LC cells on 30 °C. Finally, the LC cells were cooled to room temperature. Under a supersaturated state at room temperature, C₈-BTBT crystals were grown in the LC cells for 12 h. The residual LC solvent in the cells was removed with ethanol as an antisolvent for C₈-BTBT. Note that cell thickness and C₈-BTBT concentration for large crystal growth were optimized in a previous study [10].

Fig. 1(b) and (c) show the chemical structures of the organic semiconductor material C₈BTBT (supplied by Nippon Kayaku Co., Ltd.) and the nematic LC solvent 4-cyano-4'-pentylbiphenyl (5CB; purchased from LCC Corp.), respectively. The transition temperature of 5CB from nematic to isotropic phase is ca. 35 °C. Fig. 1(d) shows crossed-Nicol polarizing microscope images of a deposited C₈-BTBT crystal after removal of the LC solvent. Extinction behavior was observed by rotation of the polarizer. We analyze these crystals in the subsequent discussion. X-ray diffraction was carried out using an X-ray diffractometer equipped with a Cu-K α source of wavelength 1.54 Å (Smart-Lab; Rigaku). The polarized Raman spectrum was measured using a confocal laser Raman microscope (NRS-5100; JASCO Co., Ltd.) with incident laser wavelength of 532 nm.

To investigate the molecular vibration mode of a C₈-BTBT molecule, DFT calculation was performed with the Amsterdam Density Functional software package (ADF; supplied by Molsys, Inc.). The DFT calculation is based on an approximate solution of the wave function from the Kohn–Sham equation [12]. The calculated result exhibits the most stable molecular energy due to the calculation being based on the variational principle. To calculate the molecular

energy of a C₈-BTBT molecule, we used the B3LYP/6-31G(d) functional and basis set [13] for approximation.

3. Results

3.1. Structural evaluation of C₈-BTBT single crystals

3.1.1. Molecular ordering along the in-plane direction

Fig. 2 shows X-ray diffraction patterns of a C₈-BTBT crystal grown in parallel-aligned 5CB solvent, as shown in Fig. 1(d). Before X-ray measurement, the residual 5CB solvent on the C₈-BTBT crystal was removed by ethanol solvent. We analyzed the diffraction pattern based on the previously reported bulk-phase C₈-BTBT single crystal structure [8]. According to the previous report on the bulk-phase structure, the crystal *a*-, *b*-, and *c*-axis lattice constants are 5.93 Å, 7.88 Å, and 29.18 Å, respectively. To clarify the crystalline *b*-axis direction of the C₈-BTBT single crystals, we examined the φ -scan measurement at $2\theta_{\chi} = 22.15$ degrees, which corresponds to the diffraction angle from the (0 2 0) crystal plane, as shown in Fig. 2(a). In this measurement, the LC alignment direction was perpendicular to the incident X-ray beam when φ was 0 degrees. The direction of the scattering vector in the (0 2 0) crystal plane indicates the direction of the crystal *b*-axis in the C₈-BTBT crystals. Fig. 2(b) shows φ -scan data of a deposited C₈-BTBT crystal. In the crystalline C₈-BTBT grown with the 5CB solvent, two diffraction peaks of (0 2 0) at $\varphi = 31.3$ and 211.3 degrees appeared. These peaks were separated by an angular interval of 180 degrees. According to the bulk-phase single crystal structure of C₈-BTBT, as described in Ref. [8], the (0 2 0) plane has a rotational symmetry through 180 degrees. Therefore, the deposited C₈-BTBT crystals have the single crystal structure. Interestingly, two diffraction peaks appeared when the direction of the scattering vector corresponding to the crystal *b*-axis was parallel to the LC alignment direction. These diffraction patterns indicate that any directional control of the crystal *b*-axis in C₈-BTBT single crystals is realized by the rubbing-treatment direction. To investigate the dominant factor of this specific molecular orientation in C₈-BTBT single crystals, we examined the φ -scan data of a C₈-BTBT single crystal that was grown by a cell structure composed of two rubbing-treated polyimide/glass substrates and toluene solvent as non-liquid crystalline solvent (see Fig. 2(b)). A toluene-grown C₈-BTBT crystal also has single crystal structure due to angular interval of 180 degrees. As a result, the diffraction peak of the (0 2 0) plane was not consistent with the diffraction pattern of C₈-BTBT obtained by using LC solvent. Although the toluene molecules are not aligned, 5CB molecules have ordered state on rubbing-treated polyimide films. Therefore, the origin of the *b*-axis orientation along the LC alignment direction is associated with the aligned 5CB molecules. Generally, crystal nucleation occurs near substrate interface due to interface energy as driving force. We consider that aligned 5CB might be effective to orientation during crystal growth stage.

Fig. 2(c) shows $2\theta_{\chi}/\varphi$ scan data at $\varphi = 31.3$ degrees. In the case of 5CB solvent, a diffraction peak of the (0 2 0) plane was observed at $2\theta_{\chi} = 22.15$ degrees. The diffraction signal derived from the *a*-axis direction cannot be observed. The estimated *d*-spacing value from Bragg's equation was 4.00 Å. On the other hand, in the case of toluene solvent, diffraction from the (0 2 0) plane appeared at $2\theta_{\chi} = 22.54$ degrees. This diffraction angle corresponds to a *d*-spacing of 3.94 Å. These results mean that the distance between the (0 2 0) planes of LC-grown C₈-BTBT single crystals is slightly larger than that of bulk-phase C₈-BTBT single crystals. One of the reasons for this difference may be the possibility of molecular conformation changes of C₈-BTBT. For instance, alkyl chains of C₈-BTBT have angular flexibility and rotatability. In contrast, the

Download English Version:

<https://daneshyari.com/en/article/8148493>

Download Persian Version:

<https://daneshyari.com/article/8148493>

[Daneshyari.com](https://daneshyari.com)