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Single crystalline growth of a soluble organic semiconductor in a parallel aligned liquid crystal solvent using rubbing-treated polyimide films

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For directional control of organic single crystals, we propose a crystal growth method using liquid crystal as the solvent. In this study, we examined the formation of 2,7-dioctyl[1]benzothieno[3,2-*b*][1]benzothiophene (C_8 -BTBT) single crystals using a parallel aligned liquid crystal (LC) cell and rubbing-treated polyimide films in order to clarify the effects of LC alignment on anisotropic C_8 -BTBT crystal growth. Based on the results, we found that the crystal growth direction of C_8 -BTBT single crystals was related to the direction of the aligned LC molecules because of rubbing treatment. Moreover, by optical evaluation, we found that the C_8 -BTBT single crystals have a aligned molecular structure.

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1. Introduction

Solution-processed crystal growth of organic semiconductors has been investigated not only for an interest in growing crystals but also for its various applications in printed electronics such as light-emitting diodes, photovoltaics, and transistors.¹⁻³⁾ Recently, remarkable progress has been made in the area of organic semiconducting materials, e.g., the development of terminally-modified benzothienobenzothiophene derivatives C_n -BTBT ($n = 4, 8, 12$).⁴⁾ The C_n -BTBT derivatives for p-type organic transistors have attracted much attention because of their excellent hole mobility ($>1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), good solubility to solvents, layered-crystalline structure, and air stability. Based on the soluble organic semiconductor, C_8 -BTBT, the thin-film growth methods such as double-shot inkjet printing,⁵⁾ edge casting,⁶⁾ and off-center spin coating⁷⁾ have been developed. Besides, structural study of C_8 -BTBT crystals was done for understanding of high-performance organic transistors.⁸⁾ It was reported⁵⁻⁷⁾ that excellent mobility was achieved for single crystals composed of edge-on C_8 -BTBT molecules. One of the main reasons for this is that the π - π overlap among orbitals of benzothienobenzothiophene skeleton is large in C_8 -BTBT single crystals. Generally, single crystals composed of organic molecules have anisotropic carrier transport characteristics because the π - π molecular interaction among molecules is different along each crystalline axis.⁹⁻¹¹⁾ For this reason, a directional control technique for organic single crystals is required for optimizing carrier transport characteristics between source and drain electrodes. However, there has been little development in the area of solution-based single-crystal growth techniques. An optimization method is required for the fabrication of integrated circuits using organic semiconductors, such as the ones used for active-matrix displays, in order to suppress the characteristic variability.

To overcome this issue, we have focused on crystal growth using liquid crystal (LC) as the solvent. The direction of LC molecules in the nematic-phase is controllable by the electric field or polyimide alignment films. In previous papers, we reported that the single crystalline growth of organic semiconductors was possible using a nematic-phase LC solvent.^{12,13)} In the LC cell under the influence of an applied lateral electric field, the C_8 -BTBT single crystals

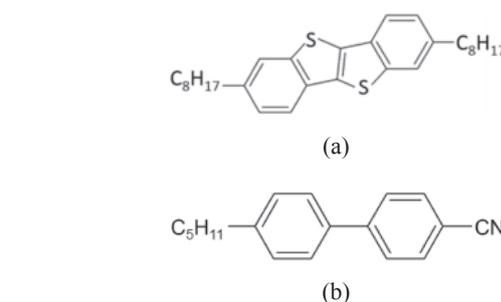


Fig. 1. Molecular structure of: (a) C_8 -BTBT and (b) liquid crystal solvent, 5CB.

exhibited anisotropic growth and a peeling behavior.^{13,14)} However, the main factor that determined the anisotropic growth direction of C_8 -BTBT single crystals, such as lateral electric field or LC alignment, was not clear.

Here, we report the single crystalline growth of the soluble organic semiconductor, C_8 BTBT, using a nematic-phase LC and rubbing-treated polyimide films. We found that the aligned LC molecules contribute to the anisotropic single crystal growth of C_8 -BTBT. The structure of deposited C_8 -BTBT single crystals was evaluated using a polarizing microscope with crossed nicols, and by optical absorption spectroscopy and X-ray diffraction (XRD) analyses.

2. Experimental methods

The organic semiconductor material and nematic LC solvent used were 2,7-dioctyl[1]benzothieno[3,2-*b*][1]benzothiophene (C_8 -BTBT; Nippon Kayaku) and 4-cyano-4'-pentylbiphenyl (5CB; LCC), respectively. Figure 1 shows the chemical structure of C_8 -BTBT [Fig. 1(a)] and 5CB [Fig. 1(b)]. The transition temperature of the nematic-isotropic phase in 5CB is ca. 35 °C. The 5CB at liquid phase becomes opaque due to light scattering below the phase transition temperature because of the multi-domain liquid crystal possessing optical anisotropy, while it becomes colorless and transparent in the isotropic phase.

The procedure for C_8 -BTBT crystal growth is as follows: The polyimide films (JSR AL1254) were spin-coated at 3000 rpm for 30 s on an ultrasonically cleaned glass substrate. Then, polyimide films were baked at 200 °C for 1 h. Next, a

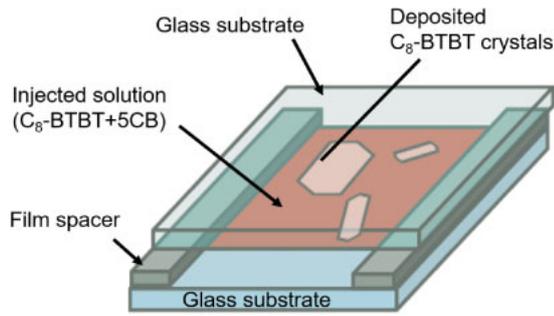


Fig. 2. (Color online) Schematic of the solution cells during crystal growth process.

rubbing treatment was carried out on the polyimide films using a rubbing machine (EHC RM-50). The conditions for the rubbing treatment were as follows: The rotation speed of the rubbing roller was 500 rpm, the diameter of its roller was 4.5 cm, the substrate carrier speed was ca. 5 mm/s, and the push length of velvet cloth to substrate was ca. 0.5 mm. We constructed the anti-parallel solution cells (via opposite rubbing directions between upper and lower substrates) using two rubbing-treated substrates to align the 5CB molecules. Prior to crystal growth, we confirmed that only 5CB exhibited parallel alignment in the cells. Note that parallel alignment of 5CB is defined as the parallel state between the molecular long axis and the rubbing direction. The C₈-BTBT solution was injected into solution cells on a hotplate at 60 °C. Finally, solution cells were cooled to room temperature (RT). Under a supersaturated state at RT, C₈-BTBT crystals were grown in solution cells for 12 h, as shown in Fig. 2. The residual LC solvent in the solution cell was removed with ethanol.

The thickness of the C₈-BTBT single crystals was evaluated using a confocal laser microscope (Keyence VK-9700). The anisotropy of the C₈-BTBT crystals was evaluated using a polarizing microscope with crossed nicols and a Berek compensator (Olympus U-CBE). Furthermore, we measured the ultraviolet–visible light absorption spectra using linearly polarized incident light and a spectrophotometer (Hitachi U-4000). X-ray diffraction was carried out by an X-ray diffractometer equipped with a Cu-K α source of wavelength 0.154 nm (Rigaku Smart-Lab).

3. Results and discussion

3.1 Solubility of C₈-BTBT in LC solvent

Figure 3 shows the solubility–temperature characteristics of C₈BTBT in 5CB solvent. The solubility is estimated as a saturated concentration of C₈-BTBT while heating and stirring the solution. The plot in Fig. 3 indicates a linear approximation at a range from 37 to 60 °C. Note that the phase of 5CB in this temperature range is isotropic. C₈-BTBT exhibits good solubility with 5CB, as much as 3.1 wt % at 37 °C, which is near the phase-transition temperature of 5CB. According to the theory of crystal growth in liquid phase, the driving force for crystal nucleation strongly depends on the degree of supersaturation d_{sup} , expressed as $d_{\text{sup}} = (C - C_s)/C_s$, where C and C_s are the concentration of solution and concentration at supersaturated state, respectively.¹⁵ For crystal growth using LC-phase 5CB under a supersaturated state at RT, the C value needs to exceed

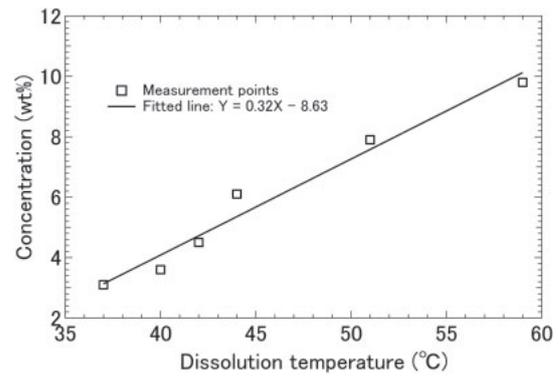


Fig. 3. Solubility characteristics of C₈-BTBT solution using 5CB solvent.

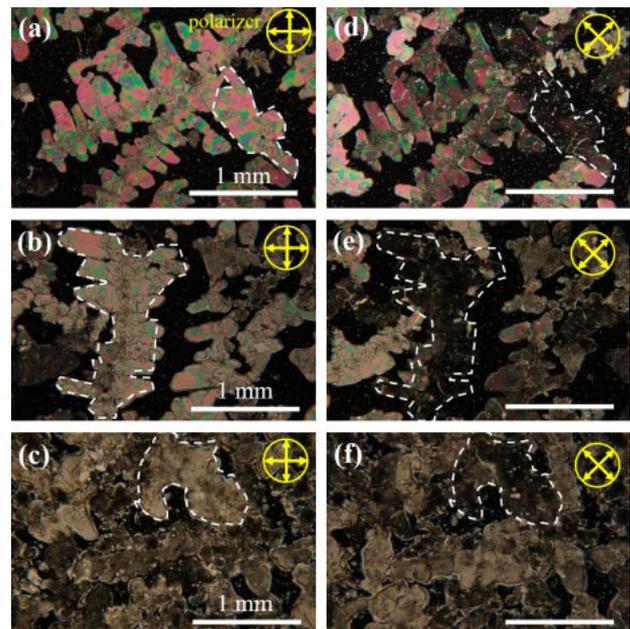


Fig. 4. (Color online) Microscope images with crossed-nicols polarizer of solution cell at 10 wt % concentration including 5CB solvent: (a, d) 11.5 μm thickness, (b, e) 25 μm thickness, and (c, f) 50 μm thickness. Note that these solution cells are composed of glass substrate without rubbing-treated polyimide films.

3 wt %. We grew C₈-BTBT crystals in the LC-aligned state at concentrations greater than 3.1 wt % at RT using solution cells.

3.2 Growth condition of C₈-BTBT single crystals

Based on the solubility–temperature characteristics, we investigated the growth condition of C₈-BTBT single crystals using 5CB solvent in glass cells (without polyimide films). Then, we prepared three kinds of glass cells that were of different spacer thicknesses: 11.5, 25, and 50 μm . Figures 4(a)–4(c) show the crossed-nicols microscope images of the solution cells at 10 wt % concentration. Note that these images were captured before the removal of the 5CB solvent. The growth of plate-like C₈-BTBT was observed regardless of spacer thickness. The solution cells of 11.5 μm thickness have inhomogeneous interference due to birefringence of the 5CB molecules. The retardation of LCs depends on both the anisotropy of the refractive index and the thickness. Therefore, optical interference as shown in Figs. 4(a) and 4(b) means that LC growth or C₈-BTBT film thickness is

inhomogeneous. Here, we discuss the black-colored regions (not shown optical interference by birefringence) in the microscopic images, as shown in Fig. 4. The regions of black color in the microscope images indicate the possibility of whether vertically-aligned or isotropic-phase LC. Generally, the nematic-phase LC molecules do not align, like vertically-aligned, in the glass cells without an alignment treatment. The images of Fig. 4 were observed at RT. Therefore, the data of microscope images is inconsistent with prediction. As one of possibilities, we considered the presence of vertically aligned LCs in the black region due to surface anchoring from ultra-thin C₈-BTBT crystals. Therefore, the glass substrate might be covered with C₈-BTBT microcrystals having inhomogeneous thickness. In the case of the thick spacer, the area of the black region decreased due to deposited C₈-BTBT films onto the glass substrate [see Fig. 4(c)].

In order to confirm the molecular alignment in these crystals, we took polarizing microscope images with the polarizer rotated by 45°, as shown in Figs. 4(d)–4(f). Extinction behavior was partly observed regardless of the film spacer thickness (the region within the enclosed white broken line). Most of the crystals do not demonstrate an aligned extinction position. In particular, solution cells having the 50 μm film spacer exhibited few extinction regions. Thick solution cells lead to stacked microcrystals. Of the three cell thicknesses, the 11.5 μm solution cells showed better growth conditions than the other cell thickness for C₈-BTBT single crystals. The deposition of microcrystals is attributed to an increase in the crystal nucleation rate in solution cells, owing to a large d_{sup} value. In order to decrease d_{sup} , we prepared the 11.5-μm-thick solution cells with an injected C₈-BTBT solution of 6 wt%. Figures 5(a) and 5(b) show the crossed-nicols microscope images of the solution cells with 6 wt% concentration after the removal of 5CB. In this growth condition, it was observed that the deposition of microcrystals was drastically suppressed. Here, the evaluated thickness of C₈-BTBT single crystals was in the range from 0.5 to 5 μm. For applications of high-mobility organic thin-film transistors, the thick films are considered appropriate for bottom-gate/bottom-contact or top-gate/top-contact structures because their structure reduces the resistance value between the channel edge and source/drain electrodes. The right and left edges as shown in Fig. 5 corresponds to the edges of the solution cells. The 5CB solvent around the edges were easily evaporated because the solution was exposed to ambient air. For this reason, the microcrystals were deposited on the edges of the solution cell. When the polarizer was rotated by 45°, as shown in Fig. 5(b), extinction behavior was also observed. The area of the crystals without grain boundary (within the enclosed white, broken line) is larger than that of the 10 wt% concentration. This is attributed to a stable crystal growth process in terms of the nucleation and crystal growth rates. Although the presence of grain boundaries in these crystals should be evaluated by atomic force microscope images, we cannot take a topography images owing to slight residual 5CB on the C₈BTBT crystal surface. In this study, we optimized the growth condition for C₈-BTBT single crystals using 5CB solvent. The optimized concentration and spacer thickness were 6 wt% and 11.5 μm, respectively.

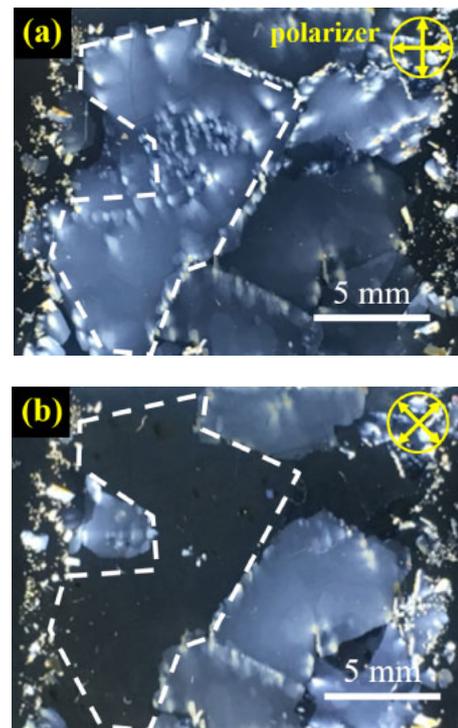


Fig. 5. (Color online) Microscopic images with crossed-nicols polarizer of solution cell at 6 wt% concentration without polyimide film: (a) polarizer 0° and (b) polarizer 45°.

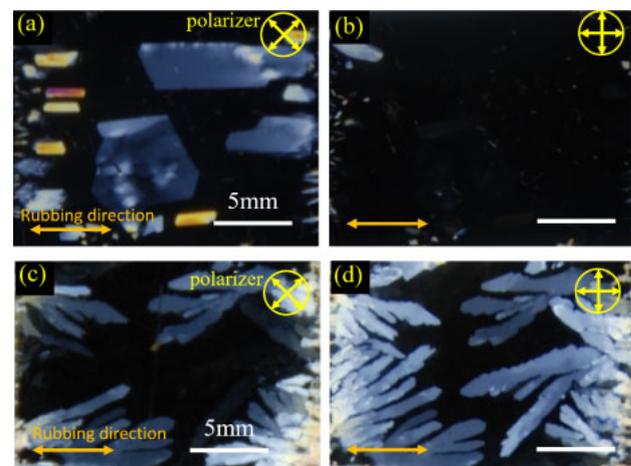


Fig. 6. (Color online) Microscope images with crossed-nicols polarizer of deposited C₈BTBT crystals with anti-parallel 11.5-μm-thick solution cells at 6 wt% concentration: (a, b) using LC solvent (c, d) using toluene solvent. Note that the 5CB solvent in these solution cells was removed using ethanol.

3.3 Effect of LC alignment on crystal growth direction

Figures 6(a) and 6(b) show crossed-nicols microscope images of C₈-BTBT crystals using anti-parallel cells having 11.5 μm thickness and 6 wt% concentration. In these microscope images, note that the optical interference cannot be observed because 5CB solvent was removed by ethanol. The maximum crystal size of 5 × 2 mm² was obtained without grain boundary. Under parallel aligned LC, crystal growth of C₈-BTBT along the rubbing direction was observed, as shown in Fig. 6(a). Compared with glass solution cells, the configuration of crystals shows a plate-like shape along the rubbing direction. In other words, the C₈-BTBT crystals in

parallel aligned 5CB showed two-dimensional anisotropic crystal growth. This specific behavior is attributed to the molecular interaction between aligned 5CB and C₈-BTBT. From the black colored region of images, as shown in Fig. 4, it was indicated that 5CB molecules on ultra-thin C₈-BTBT films had a vertical alignment. The anchoring of 5CB is attributed to van der Waals interactions between alkyl chains of C₈-BTBT and 5CB. The rubbing-treated polyimide film leads to formation of parallel aligned 5CB. There is a possibility that alkyl chains of C₈-BTBT were aligned along the rubbing direction. Also, two-dimensional crystal growth might indicate that C₈-BTBT is preferentially grown near the substrate surface. If crystal growth occurs in bulk 5CB, three-dimensional crystal growth is also predicted. Peeling of deposited C₈-BTBT crystals was difficult due to the adhesive strength between the C₈-BTBT crystals and the substrate. Indeed, peeled and movable C₈-BTBT crystals in the LC cells show three-dimensional crystal habit (they do not show a plate-like shape).¹³⁾

When the polarizer was rotated 45° from the rubbing direction, extinction positions in most of the single crystals were uniform. This behavior indicates that the specific crystalline direction of individual single crystals are aligned. To investigate the origin of anisotropic crystal growth in aligned LC solvent, we grew C₈-BTBT single crystals using toluene solvent (toluene does not show liquid crystallinity) and polyimide-coated rubbing cells. Their crossed-nicols microscope images are shown in Figs. 6(c) and 6(d). We also set the concentration of C₈-BTBT and the spacer thickness to 6 wt % and 11.5 μm, respectively. It was observed that radial crystal growth of C₈-BTBT occurred from the edge of the solution cells. Compared with 5CB, the toluene is a more volatile solvent. For this reason, the crystal nucleation at the cell edge is most likely formed by a quick solvent-drying process because the cell edge is always exposed to ambient air. Therefore, the radial crystal growth from the cell edge means that crystal growth occurs from cell edge to center. The important point is that the extinction position of C₈-BTBT single crystals is random, compared to Figs. 6(a) and 6(b). These results provide the evidence that an aligned extinction position is caused by using aligned 5CB molecules as a solvent. The growth direction of C₈-BTBT single crystals is uncontrollable using only rubbing-treated polyimide films. These findings support the presence of intermolecular interaction between C₈-BTBT and parallel-aligned 5CB molecules. Therefore, we found that the crystal growth direction of C₈-BTBT toward the in-plane direction is controllable using aligned 5CB solvent.

3.4 Optical evaluation of aligned C₈-BTBT structure

We confirmed the formation of molecular-aligned single crystals by optical evaluation. The optical slow axis, which corresponds to high refractive index, can be evaluated by a Berek compensator. The observation of extinction behavior under an optically-compensated state means formation of molecular-aligned single crystals. Figures 7(a) and 7(b) show the microscopic images with Berek compensator and polarizers of the C₈-BTBT single crystals that are aligned along the rubbing direction. When the optical slow axis of the compensator is perpendicular to that of the C₈-BTBT single crystals, the retardation of the single crystal is compensated. The extinction behavior was observed by the setting of

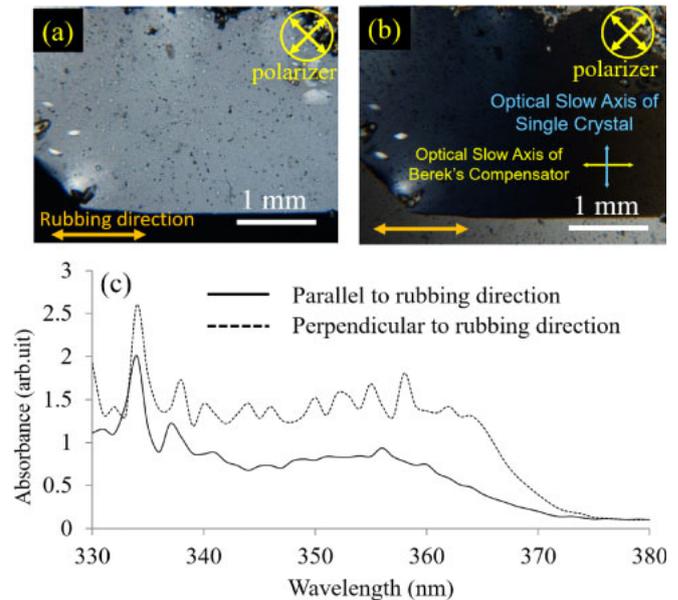


Fig. 7. (Color online) Optical evaluation of C₈-BTBT single crystals using anti-parallel solution cells. (a) and (b) are microscopic images with and without Berek compensator, respectively. (c) Polarized ultraviolet-visible absorption spectra.

ca. 80-nm retardation of the compensator, as shown in Fig. 7(b). As a result, we found that the single crystals have the aligned optical slow axis perpendicular to the rubbing direction. These results indicate that the specific direction of the crystalline axis in C₈-BTBT single crystals was aligned with the rubbing direction. In the molecular-aligned crystal structure, anisotropy of the light absorption axis can be observed because the transition dipole moment of the molecules was oriented toward a specific direction. Figure 7(c) shows the ultraviolet-visible absorption spectra of C₈-BTBT single crystals with polarized incident light. In terms of polarized direction, we compared directions that were parallel and perpendicular to the rubbing direction. The single crystals exhibited strong absorption for polarized vibrating in the direction perpendicular to the rubbing direction. In contrast, weak absorbance was observed parallel to the rubbing direction. The C₈-BTBT single crystals in parallel aligned 5CB solvent have optical anisotropy, clearly.

To evaluate the crystal structure, we performed XRD measurements on a single crystal using aligned 5CB solvent. Figure 8(a) shows out-of-plane XRD patterns in C₈-BTBT single crystals. For comparison, we exhibited the diffraction pattern of C₈-BTBT single crystals using toluene solvent. Obtained patterns were analyzed based on the single crystal structure of C₈-BTBT.¹⁶⁾ According to the literature, the lattice constants of C₈-BTBT single crystal are as follows: $a = 5.93 \text{ \AA}$, $b = 7.88 \text{ \AA}$, and $c = 29.18 \text{ \AA}$. The crystalline c -axis corresponds to molecular long axis of C₈-BTBT. The crystalline system of C₈-BTBT is monoclinic. All of the peaks can be attributed to the first and higher order (as high as ninth) diffractions from the d -spacing corresponding to the $(00l)$ plane (d -spacing was calculated using Bragg's equation). Estimated d -spacing values of the (001) planes, $d_{(001)}$, are as follows: toluene solvent, 29.1 Å; 5CB solvent, 28.6 Å. These $d_{(001)}$ values mean edge-on orientation of the C₈-BTBT molecules on the polyimide substrate because the

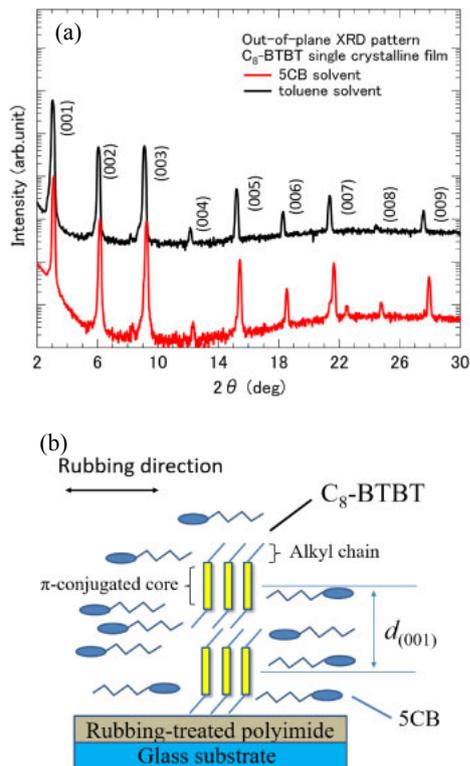


Fig. 8. (Color online) (a) Out-of-plane XRD patterns of C_8 -BTBT single crystals. (b) Schematic of C_8 -BTBT crystal structure in aligned 5CB solvent.

calculated d -spacing value is nearly consistent with the lattice constant of the c -axis, as shown in Fig. 8(b). The deposited C_8 -BTBT crystals using toluene solvent were bulk-phase single crystals. Interestingly, $d_{(001)}$ in 5CB solvent is different from bulk-phase crystals. The peak position is shifted to a wider angle in comparison to toluene. This peak shift indicates the aligned structure of the alkyl chain of C_8 -BTBT single crystals along the rubbing or 5CB alignment direction, as discussed above. G. Gbabode et al. reported that arrangement between alkyl chains of C_8 -BTBT involved the changing of intermolecular distance.⁸⁾ These results indicate that structural change of C_8 -BTBT crystals is attributed to alignment of alkyl chains because π -conjugated core in C_8 -BTBT is rigid skeleton. These diffraction patterns show that the crystalline c -axis is aligned toward the out-of-plane direction from the substrate surface. Therefore, the specific direction in the crystalline plane, composed of the a - and b -axes, is along the rubbing direction. In this study, we found that edge-on C_8 -BTBT crystals exhibited anisotropic crystal growth in aligned 5CB molecules.

4. Conclusions

We examined the formation of C_8 -BTBT single crystals using liquid crystal solvents and rubbing-treated polyimide films, and achieved control of the alignment in the deposited their crystals. The C_8 -BTBT has good solubility with 5CB, as much as 3.1 wt % at 37 °C. Resulting from the optimized

crystal growth condition, single crystals were obtained. In this study, it was verified that LC alignment as the solvent is the most important factor for determination of anisotropic single crystalline growth of C_8 -BTBT. We also found that the crystalline a - b plane or optical slow axis in edge-on oriented C_8 -BTBT single crystals is controllable by the direction of parallel aligned 5CB.

The crystal growth method using aligned LC solvent will be expected to the optimization of mobility in organic thin-film transistor devices and the suppression of characteristic variability in integrated circuits using organic semiconducting devices. For applications of semiconducting devices, some challenges remain, e.g., a method to completely remove LCs from the deposited crystal surface, a peeling technology for films, and positional control of crystal deposition to channel region. Furthermore, the origin of anisotropic crystal growth remained unclear. In the future, it will be necessary to overcome these challenges for high-performance organic thin film devices.

Acknowledgments

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