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Optimization of thermal treatment of vapor-deposited thiophene/phenylene co-oligomer films

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ABSTRACT

We evaluated the thermal crystallization of deposited films made of 2,5-bis(4-biphenylyl)thiophene (BP1T) and 1,4-bis(5-phenylthiophen-2-yl)benzene (AC5), which are thiophene/phenylene co-oligomers (TPCOs). The deposited films of both BP1T and AC5 showed a microcrystalline phase, and initial microcrystals grew 10 – 100 times with thermal treatment. The XRD profile of BP1T indicated that the thermal treatment resulted in a densely packed crystalline layer, and the XRD results for AC5 after treatment were similar to those reported for AC5 single crystals. Thermal treatment of the deposited film is an effective process to grow microcrystals of deposited films of TPCO. We inferred that one of the main mechanisms of thermal crystallization involves the strain energy, which was saved around the grain boundaries.

1. Introduction

In the last decade, single crystals of organic low-molecular weight compounds have attracted a great deal of attention because of their highly ordered state, resulting in excellent electronic and photonic performance [1–3]. The regular arrangement of their molecules is responsible for high carrier transport mobility [4,5], polarized emission, and spectrally narrowed emission [6]. Therefore, demand for these crystals has been increasing, and many crystal growth techniques have been proposed and developed. Among these crystal growth techniques, the vapor phase method under environmental gas at high pressure allows preparation of relatively large single crystals of low-molecular weight compounds [7–10]. Kloc et al. obtained single crystals of oligothiophene derivatives by this method [9]. Ichikawa et al. also made millimeter-sized single crystals by a similar simplified method [10]. However, as these methods cannot permit crystals onto accessible substrates, each single crystal obtained by these methods must be placed on an appropriate substrate, such as indium tin oxide (ITO), SiO_2/Si, etc. Furthermore, it takes more than 20 h to obtain a suitably sized crystal.

On the other hand, the high-temperature vapor deposition method was proposed for the preparation of crystal films on various substrates. The crystal films of thiophene/phenylene co-oligomers (TPCOs) prepared by high-temperature vapor deposition were applied for field effect transistors (FETs) [11]. However, the crystal domain sizes of the resulting films were not adequately large, and it is necessary to form larger crystal domains of deposited films on the substrate.

Recently, we applied the thermal treatment process to evaporated films for development of electronic and photonic devices. This process allows coverage of the organic compound onto the whole surface of a patterned substrate and also enables us to crystallize the evaporated film on the patterned electrode. Furthermore, local and rapid heating can be achieved in place by spot heating processes, such as pulsed laser irradiation. Therefore, it is essential to optimize the crystallization conditions of the evaporated films.

Here, we report the thermal crystallization behavior of vapor-deposited TPCO films prepared at room temperature, and discuss the possibilities and optimum conditions for thermal treatment.

2. Experimental section

The TPCOs used in the present study were 2,5-bis(4-biphenylyl)thiophene (BP1T) and 1,4-bis(5-phenylthiophen-2-yl)benzene

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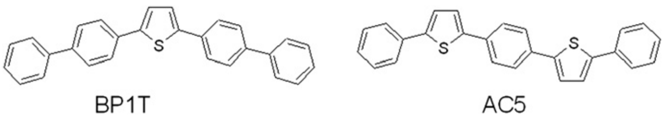

Fig. 1. Chemical structures of TPCOs used in the present study. Left, BP1T; Right, AC5.

(AC5), the chemical structures of which are shown in Fig. 1. Vapor deposition of these compounds was carried out onto the SiO_2 substrate covered with a fluorinated polymer, Cytop (CTX809A; Asahi Glass Co. Ltd) by spin-coating and post-heating. Cytop has good transparency, a low surface energy, and thermal stability; thus, we anticipated that it can play a role as a better auxiliary material to make larger crystal domains with thermal treatment. Vapor deposition rate was 0.08 – 0.15 nm/s under reduced pressure of several 10^{-6} Pa. The deposition films had a final thickness of approximately 500 nm.

The morphologies of these deposition films were examined under a polarizing microscope (Olympus Model BH-SP) equipped with a hotstage (Models FP-80; Mettler Co. Ltd.) Thermodynamic properties were determined with a differential scanning calorimeter (DSC; PYRIS DIAMOND DSC; Perkin Elmer Co. Ltd.) at a heating rate of 10 °C/min. The X-ray diffractions were measured with a RIGAKU RU-300 X-Ray diffractometer and Cu-Kα radiation.

3. Results and discussion

3.1. Morphologies

Fig. 2 shows DSC curves of the vapor deposited film of BP1T, and this profile was the first heat scan for the BP1T film deposited at room temperature. A single endothermic peak was observed at around 334 °C corresponding to the melting point of BP1T. Vapor-deposited films of organic low-molecular weight compounds used in electroluminescent (EL) devices, such as N,N'-diphenyl-N,N'-bis(3-methylphenyl)-4,4'-bianiline (TPD) and Tris-(8-hydroxyquinoline)aluminum (Alq_3), show an amorphous state, and they can change from an amorphous to a crystalline state by absorbing heat, so that endothermic curves due to glass transition and the exothermic peak for crystallization are found in their DSC curves [12]. We first assumed that the morphology of the evaporated BP1T film was amorphous. As vapor deposition of the films in the present study was performed at room temperature, sublimed molecules would dissipate their energy based on thermally activated molecular vibration into the substrate. This causes freezing of the molecular motion resulting in an amorphous state on the substrate. Our assumption was different from the result; however, other researchers also described evaporated films as being in the amorphous state in similar studies; naturally, they did not confirm the morphologies of TPCO samples with a polarizing microscope and/or DSC. As described below, thermal treatment of BP1T was performed from 170 °C to 235 °C, and no endothermic or exothermic peak was observed in this temperature region of the DCS curve.

Fig. 3 shows photomicrographs of vapor-deposited BP1T films under crossed nicols. The deposited films were also confirmed to be in the microcrystalline state and not in the amorphous state. In terms of crystallization in the vapor phase method described in the Introduction section [4], as the substrate is heated as well as the source zone, the molecules of vaporized materials do not lose most of their vibrational energy on contact with the substrate. Therefore, molecules with large vibrational energy aggregate into the crystalline state onto the substrate.

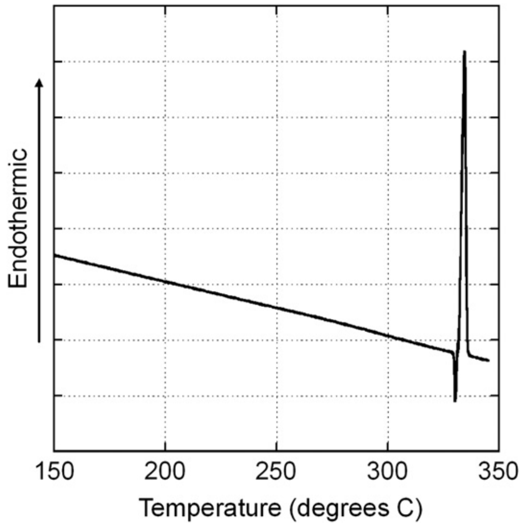

Fig. 2. DSC curve of vapor-deposited film of BP1T.

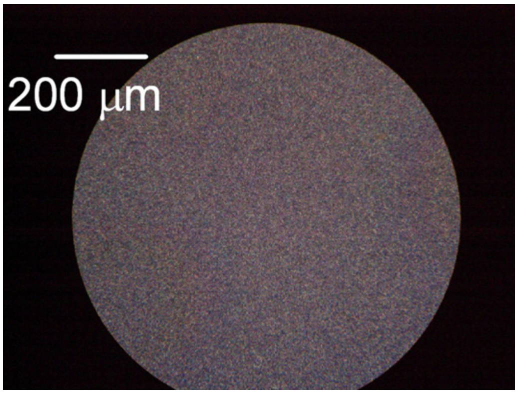

Fig. 3. Polarizing micrograph of BP1T under crossed nicols.

3.2. X-ray diffraction

Fig. 4 shows X-ray diffraction (XRD) profiles of deposited BP1T films with a series of thermal treatments: before treatment, during treatment, and after treatment. Thermal treatment was performed at 190 °C. The XRD profiles of untreated BP1T films showed relatively high-order reflection up to the sixth order, which was well-resolved. This result was responsible for its layered structures consisting of the vertical molecular alignment. Two non-ordered peaks at 19.4° and 23.4° were also observed, as reported previously. Hotta et al. reported that the peaks at 19.4° and 23.4° were due to lateral separation between the nearest-neighbor molecules and represented partial molecules lying parallel to the substrate [13].

In the case of BP1T films during thermal treatment, the intensities of all peaks decreased in comparison with those before thermal treatment. This phenomenon is attributed to fluctuations in molecules with thermal motions. Furthermore, all the ordinary peaks shifted to higher angles by approximately 1°. The higher angle shift seems to cause denser molecular packing, and thermal treatment was shown to move molecules gradually into an ordered state. On the other hand, the non-ordered peaks at 19.4° and 23.4° did not shift to higher angles. This result indicated that the parallel alignment in a minor part of this system does not lead to denser packing. Finally, after thermal treatment, these two peaks disappeared completely, and ordered peaks remained shifted by approximately 1°. Hibino et al. reported that samples