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Fabrication and Characterization of Orientation-Controlled Thin Films of Distyryl Benzene Derivatives

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Fabrication and Characterization of Orientation-Controlled Thin Films of Distyryl Benzene Derivatives

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Distyryl benzene derivatives (DSB-1 and DSB-2) were deposited on a KBr (001) surface. DSB-1 molecules took two kinds of orientations depending on the substrate temperature. On the other hand, DSB-2 grew epitaxially. The longitudinal axes of DSB-2 molecules were oriented parallel to the substrate surface.

Keywords: distyryl benzene derivatives; TEM; AFM; epitaxy

INTRODUCTION

Since the first report of organic light-emitting diodes in 1987 by C.W.Tang^[1], optoelectronic devices based on organic and polymer thin film has been attracted much interest and studied extensively due to their potential applications. The characteristics of organic optoelectronic devices are heavily dependent on the structure and morphology of the film^[2,3].

In this study, two distyryl benzene derivatives which are model compounds of polyphenylenevinylene were deposited on a substrate from the vapor phase. Morphology and molecular orientation of the film were investigated by atomic force microscope (AFM) and transmission electron microscope (TEM).

EXPERIMENTAL

Distyryl benzene derivatives used were 1,4-di-*p*-methoxystyrene benzene (DSB-1) and 1,4-di-(*p*-methoxystyrene)-2,5-dimethoxybenzene (DSB-2). Their molecular structures are shown in Fig.1. They were evaporated on a fused silica glass (quartz plate) and an air-cleaved (001) surface of KBr from a fused silica crucible heated by a tungsten coil.

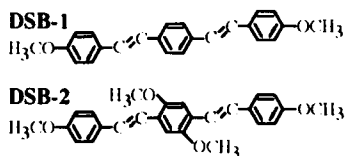


FIGURE 1 Molecular structures of DSB derivatives used.

RESULTS AND DISCUSSION

Figure 2 shows the ultraviolet-visible (UV-VIS) spectra of DSB-1 and DSB-2 films deposited on a quartz plate. DSB-1 film showed the absorption peaks at 245 nm and 295 nm. The absorption peaks of DSB-2 film shifted to longer wavelength region at 330 nm, 418 nm and 450 nm by the introduction of methoxyl groups into central benzene ring.

The DSB films deposited on a quartz plate kept at 20°C were composed of randomly oriented crystallites. On the other hand, the DSB-1 film deposited on a KBr substrate kept at 20°C showed two kinds of crystal habits, needle- and corn-like, as shown in Fig.3. The needle-like crystals were predominant and grew crossing each other orthogonally. The long axis of the crystal was parallel to either the [100] or the [010] direction of the substrate. The electron diffraction (ED) patterns of needle- and corn-like crystal displayed the single net patterns with the diffraction spots corresponding to the lattice spacings of 2.13 nm and 0.67 nm crossing each other at an angle of 70°, and those of 0.42 nm and 0.33 nm, respectively. The unit cell dimensions of the DSB-1 crystal were evaluated as $a=2.13$ nm, $b=0.83$ nm, $c=0.67$ nm and $\beta=69.5^\circ$. Figure 3(b) shows an AFM image of the film deposited

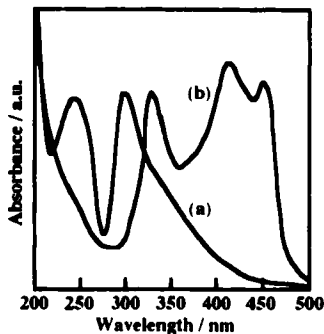


FIGURE 2 UV-VIS spectra of DSB-1(a) and DSB-2 (b) films.

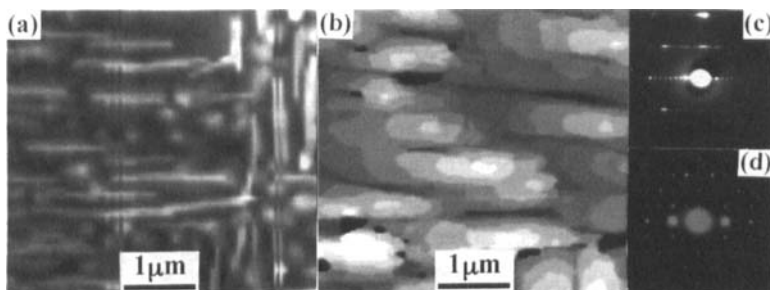


FIGURE 3 AFM images of the DSB-1 film on a KBr substrate at 20°C (a) and 100°C (b) and the ED patterns of needle-like (c) and corn-like crystals (d).

on a KBr substrate kept at 100°C. The corn-like crystals changed to the rod-like crystals along the $\langle 100 \rangle$ directions of the substrate crystal. Each crystal revealed that the multilayered structures and microcrystals with flat terraces separated by step. Each step has about 2.10 nm in height, which correlates with the length of one DSB-1 molecule. This finding suggests that the longitudinal axis of DSB-1 molecule is oriented almost perpendicularly to the substrate surface. Figure 4 shows an AFM image and an ED pattern of the DSB-2 film deposited on the KBr substrate kept at 20°C. DSB-2 also grew epitaxially forming the rectangular crystals whose long axes aligned to the $\langle 100 \rangle$ directions of the substrate crystal. The ED pattern of each crystal showed the single net pattern with the diffraction spots corresponding to the lattice spacings of 1.26 nm and 1.25 nm crossing each other at an angle of 103° . When the DSB-2 was evaporated on the substrate kept above 50°C, any film did not be formed due to the re-evaporation.

Figure 5 represents the molecular orientation of DSB-1 on the KBr substrate. In lamellar crystal, DSB-1 molecules are oriented almost perpendicularly to the substrate surface and aligned to the $\langle 100 \rangle$ directions of the substrate. In needle-like crystal, on the other hand, the longitudinal axes of DSB-1 molecules are oriented

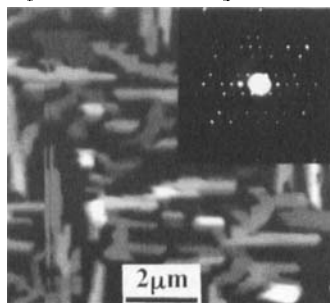


FIGURE 4 AFM image and the ED pattern of the DSB-2 film on a KBr substrate kept at 20°C.

parallel to the substrate surface. The crystal structure and molecular orientation of DSB-2 could not be determined by TEM and AFM investigations. However, the polarized fluorescence spectra of the DSB-2 film showed the anisotropic response. When the electric vectors of excitation and emission were parallel, the stronger photoluminescence (PL) was observed around 480nm. The PL intensity was very weak, on the other hand, when the electric vectors were normal. This indicates that the transition moments of the DSB-2 molecules are aligned parallel to the surface of the substrate. Since the transition moment of the lowest singlet exciton associated with $\pi - \pi^*$ band-gap was parallel to the main chain in π -

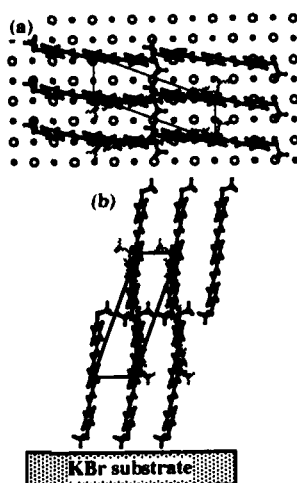


FIGURE 5 Orientations of the DSB-1 molecules in needle-like (a) and corn-like crystals (b).

conjugated polymers such as polyacetylene and poly-*p*-phenylene, the transition moment of DSB-2 seems to be parallel to the longitudinal direction of the molecule. Therefore, the longitudinal axes of DSB-2 molecules oriented parallel to the surface of the KBr substrate like as DSB-1 molecules in needle-like crystal. We are now investigating the optical properties of the films. The relationship between molecular orientation and these properties will be described in detail elsewhere.

Acknowledgments

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